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JUBILEE COMMEMORATIVE REVIEW

The Silver Jubilee of His Majesty King George V has evoked among the British people such a manifestation of the esteem in which the Royal Family is held as has never before been witnessed. All classes, professions and trades unite in a common tribute of loyalty and affection.

The past twenty-five years have been marked by unparalleled advances in science and technology. The Jubilee has been a fitting occasion to review those achievements in every field of endeavour. In the petroleum industry the development has been of outstanding importance, and it is a matter of justifiable pride that British technologists have contributed so largely to the growth of the petroleum industry in all parts of the world.

By a happy coincidence the Institution itself comes of age in this Jubilee Year. Established in 1914, the Institution was twenty-one years old on March 3rd, 1935. To mark this occasion, doubly auspicious for the Institution, the Council has agreed to the publication in June of an authoritative record of developments in the science and technology of petroleum from 1910 to 1935. The Institution has received many messages of greetings and good wishes on its coming of age from the leaders of the world's petroleum industry, and these also will be incorporated in the Jubilee Commemorative Review.

It was felt that members would like to preserve such a record in permanent book form. " Twenty-Five Years' Retrospect " will therefore be published separately and in a binding distinct from that of the monthly *Journal*. The book will be posted to all members at the same time as the June issue of the *Journal*.

NOTICES.

The Institution as a body is not responsible for the statements of opinion expressed in any of its publications.

Copyright.—Publication of abstracts of Papers and articles appearing in the Journal is permitted, provided that acknowledgment is made to the Institution of Petroleum Technologists.

Papers and Articles.—The Council invites Papers and Articles both for reading at Ordinary Meetings of the Institution and for publication in the Journal. All Papers, whether for reading or publication, will be submitted to a referee appointed by the Publication Committee.

The Institution has published a brochure "Instructions for the Guidance of Authors" containing details of recommended practice in the preparation of Papers for publication. Copies of this brochure will be supplied on request.

Pre-Prints.—Advance proofs of Papers to be read at Ordinary Meetings are generally available about a week before the Meeting. Members wishing to be supplied with these pre-prints are requested to notify the Secretary.

Abstracts.—Members and Journal Subscribers desirous of receiving the Abstracts printed on one side of the paper only, can be supplied with these at a charge of 10*s.* per annum per copy, payable in advance.

Issue of Journal.—Members whose subscription is not in arrear receive the Journal free of cost. A member whose subscription is not paid by March 31st of the year for which it is due is considered to be in arrear.

Changes of Address.—Members are requested to notify any change of address to the Secretary.

Benevolent Fund.—The Benevolent Fund is intended to aid necessitous persons who are or have been members of the Institution, and their dependent relatives.

The Fund is raised by voluntary annual subscriptions, donations, and bequests, and all contributions should be sent to the Secretary of the Institution at Aldine House, Bedford Street, London, W.C. 2. The Fund is administered by the Council through the Benevolent Fund Committee, and all applications in connection therewith must be made on a special form which can be obtained from the Secretary of the Institution.

Appointments Register.—A register of members requiring appointments is kept at the offices of the Institution, and every effort is made to assist members of the Institution in search of employment.

Members who desire their names and qualifications to be included in this register are requested to apply to the Secretary for the Form of Application for Registration, if they have not already done so. Members residing in the London area are asked, if possible, to return this Form in person and make themselves known, together with their requirements, to the Secretary. It is also requested that members should notify the Secretary immediately they have obtained an appointment.

In submitting names of candidates to prospective employers it is understood that the Institution accepts no responsibility and gives no guarantee.

Library.—The Institution's Library may be consulted between the hours of 9.30 a.m. and 5 p.m. daily. (Saturdays, 9.30 a.m. to 12 noon.)

NEW MEMBERS.

The following have been elected or transferred, subject to confirmation in accordance with By-Laws, Sect. IV, paras. 14–15, since the last issue of the *Journal*.

Members.

Mardall, Evelyn George Campbell	Trinidad.
Voogt, George	Hamburg.
Weymarn, Paul von	Oslo.
Whitney, James Gillis	Harrow.

Transfer to Member.

Tett, Hugh Charles	London.

Associate Members.

Clark, Joseph	Upper Burma.
Keplinger, C. H.	U.S.A.
Weatherill, Fred	London.
Webb, Terence Augustus	Assam.
Wigley, Ernest Robert John	Rochester.

Transfer to Associate Member.

Fraser, Norman Colin	Westcliffe-on-Sea.

Associate.

Merryweather, Herbert Sydney	Aruba.

NOMINATIONS FOR MEMBERSHIP.

The following nominations for membership of the Institution of Petroleum Technologists were approved by the Council on 14th May, 1935, and the application forms may be seen at the offices of the Institution.

The names of the Proposer and Seconder are given in parentheses.

As Members.

Hill, J. Bennett, Manager of Development Department, Sun Oil Company, Marcus Hook, Pa., U.S.A. (T. G. Delbridge; A. E. Dunstan.)

Jacomini, Virgil Victor, Petroleum Engineer, c/o The TVP Corporation, 90, West Street, New York, U.S.A. (C. S. Snodgrass; C. E. Spearing.)

Paterson, Robert Crawford, Engineer, "Strathyre," The Avenue, Royston Park, Hatch End, Middlesex. (Harold Moore; W. W. Watt.)

As Transfer to Members.

Evans, Percy, Geologist, Sunnyside, Lyminge, Folkestone, Kent. (T. Dewhurst; B. J. Ellis.)

Reynard, Herbert Corner, Research Chemist, 38, Crooks Barn Lane, Norton-on-Tees, Co. Durham. (J. Kewley; K. Gordon.)

Samuel, David Leo, Chemist, 89a, Wrottesley Road, Willesden, London, N.W. 10. (J. S. Jackson; John Parrish.)

As Associate Members.

Cock, Jens Nielsen, Partner in Lubricating Oil Firm, P.O. Box 52, Bekkelaget, near Oslo, Norway. (H. M. Wells; J. E. Southcombe.)

Halpin, Joseph James Anthony, Lubrication Engineer, Irish Shell, Ltd., 21, Dame Street, Dublin. (R. G. Strickland; J. S. Jackson.)

Macdonald, George Anderson, Lubrication Engineer, Belfast Road, Comber, Co. Down, Northern Ireland. (R. G. Strickland; W. E. Gooday.)

McLea, John Hunter, Chemical Oil-Refining Plant Superintendent, Bungalow 41, c/o Trinidad Leaseholds, Ltd., Pointe-a-Pierre, Trinidad, B.W.I. (B. G. Banks; E. C. Scott.)

Kay, John, Engineer, c/o The Burmah Oil Co., Ltd., Khodaung, Upper Burma. (G. W. Lepper; T. J. F. Armstrong.)

APPLICATION FORMS FOR ADMISSION.

The Council desire to direct the attention of members who Propose or Second an Application Form for admission to the Institution to the importance of sending a covering letter for the guidance of the Election Committee.

PERSONAL NOTES OF MEMBERS AND SPECIAL NOTICES.

It is suggested that members send information regarding their movements to the Secretary, for insertion under this heading.

Mr. A. G. V. BERRY has returned to Trinidad.

Mr. J. C. DANIEL is going to the Gold Coast Colony.

Mr. LEWIS MCL. DRADER has left Rumania, and is now in U.S.A.

The Secretary would be glad to learn of the addresses of the following members: J. M. BROWN, G. C. K. DUNSTERVILLE, M. JAWAD JAFAR, J. CECIL JONES, P. B. M. LINTON, A. MACLEAN, B. F. N. MACRORIE, W. J. REYNOLDS, W. MCKECKNIE ROBSON, K. A. SPEARING, G. S. URQUHART, and A. C. VIVIAN.

SUMMER MEETING.

The Summer Meeting of the Institution will be held on Friday, 21st June, at the Royal Society of Arts, John Street, Adelphi, W.C. 2. The Reports on the Progress of Naphthology, published in the May and June issues of the *Journal*, will be presented for discussion.

Programme.

Morning Session: 10.30 a.m. to 12.30 p.m. Chemical and Refining Section. Chairman: Dr. A. E. Dunstan, D.Sc.

Afternoon Session: 2.30 p.m. to 4.30 p.m. Geological and Production Section. Chairman: T. Dewhurst, Esq., A.R.C.Sc.

It is particularly hoped that overseas members of the Institution who are at present on leave in this country will endeavour to attend the Summer Meeting.

JUBILEE BANQUET.

The Jubilee Banquet of the Institution will be held at the Park Lane Hotel on the evening of Friday, 21st June, 1935.

The President and Lady Cadman will receive members and guests from 7 to 7.30 p.m.

Members may invite ladies.

Members will be pleased to learn that the guests who have promised to attend the Jubilee Banquet will include Sir Robert S. Horne, G.B.E., K.C., M.P.

The price of tickets for the Jubilee Banquet is 12*s.* 6*d.* each, exclusive of wines (double ticket 25*s.*), and application should be made to the Secretary of the Institution not later than 14th June. Students 7*s.* 6*d.*

STUDENTS' SECTION.

The Annual Open Meeting of the Students Section (London Branch) will be held at the Royal Society of Arts, John Street, Adelphi, W.C. 2, on Monday, June 3rd, at 6.15 p.m. Tea and light refreshments will be served from 5.30 p.m.

Mr. ALAN E. L. CHORLTON, C.B.E., M.P. (Past President, The Institution of Mechanical Engineers), will give an Address on:

"Possible Improvements in Economy with Explosion Type Engines."

The Meeting is open to all, and is particularly intended for the junior members of the staffs of the oil companies, and Students at technical institutions and colleges. Members of the Institution are asked to direct the attention of the younger men to this meeting, which will afford an opportunity of their being brought into touch with the activities of the Students Section of the Institution.

PERSIAN BRANCH.

The Annual General Meeting of the Persian Branch was held on the 30th January, 1935, at Abadan, South Iran. The following were elected Members of the Branch Committee for the ensuing year:—

Chairman: E. C. BREWSTER.
Hon. Secretary: C. V. RUTHERFORD.
Other Members of Committee: R. E. ADLINGTON, B.Sc., A.C.G.I., D.I.C.
G. L. KENNABY, B.Sc., F.C.S.
A. REID.
H. W. RIDDEN, B.Sc., A.I.C.
G. E. WHEELER.

BURMA BRANCH.

The newly formed Burma Branch of the Institution held two successful meetings on 28th February and 22nd March respectively. At the former Mr. W. E. V. Abraham gave an Address on "Oil Winning," and at the latter Mr. P. Evans gave a paper on "Drilling and Fishing under Pressure at Masimpur, Assam," which was followed by an interesting discussion.

Approximately 50 persons were present at each meeting, and the membership roll of the Branch is now 67.

CONTENTS OF JUNE JOURNAL.

The following Papers will be included in the June issue of the *Journal*:

Reports on the Progress of Naphthology, 1934 (*cont.*) :—
Refining and Chemical Section (*cont.*).
Geology and Geophysics.
Field Technology.

ARTHUR W. EASTLAKE.
Honorary Secretary.

OBITUARY.

Walter Henry Coleman.

We regret to report the sudden death of Mr. W. H. Coleman at his home in Ealing on 3rd April, 1935.

Mr. Coleman was Chief Chemist to the National Benzole Co., Ltd., from 1923 until 1930, after which he held the appointment of Consultant Chemist to the same Company.

As recently as 31st December, 1934, Mr. Coleman retired on pension, and it is sad to think that he had such a short time in which to enjoy his well-earned leisure and to follow up his many interests.

Born in Dover, Mr. Coleman was educated at Dover College, and subsequently became a schoolmaster in the North of England. Later, he joined the staff of The Gas Light & Coke Company, at Beckton, and then was for many years with Messrs. Hardman & Holden, Ltd., of Manchester. Prior to his appointment with the National Benzole Co., Ltd., he was for a number of years a Director of a Chemical Company in Scotland.

Mr. Coleman was an acknowledged authority on all matters appertaining to Tar and Tar Products, and was intimately connected with the production of Benzole in the very early days of the industry.

He was a member of the Institution from 1924 to 1934, and was frequently to be seen at our meetings, particularly in the years before 1930. He leaves a widow and three daughters, to whom we extend our deepest sympathy.

Mr. Coleman would have been 71 years of age this summer.

A. K. Steel.

REPORTS ON THE PROGRESS OF NAPHTHOLOGY, 1934.

CHEMICAL AND PHYSICAL REFINING.

By G. R. Nixon, A.R.C.S., B.Sc. (Member).

During the year 1934 there have been no outstanding advances in the refining of petroleum and its products by physical and chemical means, but rather a steady development of the various methods of acid treatment, dewaxing, and solvent extraction. There has been the usual crop of patents covering refining methods which are more of scientific than of industrial value, particularly with regard to the refining of cracked distillate. The publication of *Foreign Petroleum Technology* in 1933, and the inclusion in *Chemical Abstracts* of more abstracts of Russian journals, have shown to a wider public the trend of refining methods in U.S.S.R.

Gas.

The removal of hydrogen sulphide from gas by the Thylox process is described by Gollmar.[1] The gas is washed by an aqueous solution of sodium or ammonium thioarsenate which absorbs H_2S quantitatively. This solution can be regenerated by absorption of oxygen, which replaces and precipitates the sulphur in elemental form. The course of the reactions is given by the following equations :—

$$Na_4As_2S_5O_2 + H_2S = Na_4As_2S_6O + H_2O :$$
$$Na_4As_2S_6O + H_2S = Na_4As_2S_7 + H_2O :$$
$$Na_4As_2S_7 + O = Na_4As_2S_6O + S :$$
$$Na_4As_2S_6O + O = Na_4As_2S_5O_2 + S.$$

Sulphur compounds may also be removed from gases by circulation through an aqueous solution or suspension of a metal oxide, hydroxide, or carbonate,[2] and free sulphur recovered from the spent solution by aeration with simultaneous regeneration of the solution.

Crude Petroleum.

The refining of crude oil receives little serious attention to-day, but the following observations are of interest. According to Berger,[3] McPherson (Kansas) crude contains approx. ¼ lb. salts per brl. held in the oil and protected by a coating of paraffin or asphalt. Water washing was ineffective, and treating agents were expensive. This salt deposited in the heat exchangers of the distillation unit, and reduced the length of run. The problem was solved by flashing off the last traces of water from the crude in the debutanizer, and thus, keeping the salt in the body of the oil, it did not deposit in the heat exchangers and other important parts. The pretreatment of Baku crude oils with caustic soda (4 per cent.) at 65–70° C. is

described by Velikovskii and Druzhinina.[4] The treated crude had a lower acidity, and increased stability towards distillation and an improved colour. The caustic sludge had a high acid number and contained naphthenic acids, asphaltenes, resins and oil—in several instances emulsions were formed. According to Lazar and Evans,[5] phenols and naphthenic acids can be removed from uncracked topped crude oil by heat treatment at 315–400° C. and atmospheric pressure, under which conditions these bodies decompose.

Gasoline.

(a) *Desulphurisation.*—The removal of free sulphur from gasoline has been studied by Espach, Blade and Rue,[6] who found that a reagent prepared by bubbling H_2S through an aqueous calcium oxide slurry was capable of removing elemental sulphur, although it produced troublesome emulsions. The liquid decanted from this slurry was more effective in sulphur removal, and did not form emulsions. The efficiency of the reagent was roughly proportional to the amount of H_2S added. The reagent deteriorated on standing for one month, and had but little effect on the sulphur compounds in the gasoline. The continuous "doctor" treating of straight and cracked gasoline from North Texas and Panhandle crude is described in an anonymous article.[7] The treating plant is an integral part of the vapour recovery unit handling vapours from the distillation and cracking system and works under process pressure. The two gasolines are separately treated, and mixing with the doctor solution takes place in an 11-plate contacting column, whilst separation of the spent doctor is accomplished in two or three vertical settling columns. When the spent doctor needs regeneration, it is withdrawn from the system, heated to 180° F. and blown with air until it is a dark red and free from suspended matter; it is then made up to strength by addition of small quantities of caustic and litharge. According to Read and Hulse,[8] the emulsion layer that forms between gasoline and spent doctor contains, on an average, 60 per cent. gasoline, and a 99 per cent. recovery of this gasoline can be obtained by putting this emulsion through a low-speed Laughlin centrifuge, despite variations in its composition. According to Fischer,[9] "doctor" sludge can be regenerated by centrifuging the sludge to give PbS in one zone and oil and sodium plumbite in a second zone, which can be further separated by a baffle, and the plumbite solution be regenerated by known means.

Various modifications of the "doctor" reagent continue to be studied, and the following may be noted: sodium plumbite containing ferrous oxide or hydroxide,[10] "doctor" followed by hydrogen peroxide,[11] a suspension of lead sulphide in caustic soda,[12] a mixture of sodium silicate and litharge containing silicic acid,[13] a mixture of calcium hydroxide and lead monoxide,[14] sodium plumbite followed by an aqueous solution of cupric chloride,[15] which precipitates the oil-soluble lead compounds, and sodium plumbite, followed by a soluble sulphide and a finishing treatment with an adsorbent.[16]

The desulphurisation of cracked distillates by treatment with alkali metals under 150 lb. pressure at 350–650° F. has been patented by Sullivan and Brown [17] and by Ruthruff,[18] whilst Morrell [19] suggests the use of ferric chloride with the alkali metal. Desulphurisation in the liquid phase by use

of liquid ammonia has also been patented.[20] The use of copper salts for sweetening continues to attract attention, and the various combinations reported are: copper plus zinc silicates[21]; copper sulphate plus sodium chloride[22] in aqueous solution; percolation through brucite then through an earth impregnated with cupric chloride[23]; and copper sulphate plus ammonium chloride followed by fuller's earth percolation.[24]

The use of alkali hydroxides and carbonates in aqueous or alcoholic solution, with or without alkaline-earth oxides and sulphides, arsenious oxide, etc., is the subject of a number of patents,[25, 26, 27, 28, 29] According to Malisoff,[30] desulphurisation of gasoline can be obtained by treatment with 0·5–4 per cent. aluminium chloride at 100–150° C., while Levine[31] finds that sulphur compounds are removed from gasoline by treatment with a ketone, *e.g.* acetone, in the presence of aluminium chloride or zinc chloride. Desulphurisation of distillates in the vapour phase can be accomplished by the following methods—by passage through a tower containing alternate layers of fuller's earth and copper oxide[32]; by contact with silica gel,[33] the sulphides decomposing to H_2S; by contact with sodamide[34] or metallic nitrides[35]; by injection of ammonium sulphide[36] in the vapours before condensation; by treatment at 250° F. with a gas containing oxygen and ammonia in the presence of activated carbon[37]; by treatment with hydrogen at an elevated temperature in the presence of phosgene and in contact with charcoal[38]; or by passage with hydrogen over a molybdate catalyst at 200–450° C. under pressure.[39]

(b) *Chemical Refining.*—The most important subject in this section is the sulphuric acid treatment of cracked distillates. Cooke and Hayford[40] describe the C. W. Stratford process, which is a multi-stage quick contact operation followed by centrifugal separation, conducted on the counter-current principle. The raw distillate is treated with sludge acid in the first stage, and passes immediately to the centrifuge, where the sludge is separated and removed from the system. In the second stage the distillate is contacted with either fresh acid or sludge from the following stage. The number of stages depends on the type of distillate treated and the product desired. It is claimed for this process that there is minimum loss of octane value, and of gasoline and a maximum desulphurisation effect; it is commercially operated. The rôle of the time factor in the acid treatment of Rumanian pressure distillate has been studied by Sager[41]—the treatment was carried out at about 20° C. in a turbo-mixer working at different speeds and for different contact times, while the instantaneous separation of sludge and oil was effected in a De Laval S–N acid sludge separator. It was found that for the elimination of diolefins and the more unstable olefins 5 to 25 seconds' intimate contact was sufficient. The amount of acid influenced the contact time—with more acid it could be on the lower side, and vice versa. The rate of olefine polymerisation was high up to 80 seconds, but was retarded from 80 to 100 seconds then became approximately constant. The polymerisation losses were between 1·8 and 5·5 per cent. for long contact and 0·6–1·1 per cent. for short contact times. The same investigator[42] has isolated an inhibitor from Rumanian pressure distillate and applied it to selective acid treatment. The P.D. was treated with 2 per cent. by weight of acid in the above-mentioned apparatus, and the contact time was varied from 5 to 300 seconds. The P.D. was neutr-

alised with water and soda and steam distilled to give a gasoline of 198° C. end-point. The gasoline was tested for gum and oxidation test before and after washing with soda or doctor solution. The results showed that copper dish gum was lower the longer the contact time, whilst the Voorhees–Eisinger oxidation test tended to show the opposite. According to the former, test-soda or doctor treatment improved the gasoline. Pretreatment of the P.D. with soda before acid treatment gave, for corresponding contact times, a gasoline which showed a higher copper dish test whether it was unwashed or doctor or soda washed—again the Voorhees–Eisinger test gave the opposite effect. It was concluded that the pre-soda treatment removed phenols that had an inhibitory action on the instability of the subsequently refined gasoline. Phenols were separated from the soda extract, and shown to be suitable inhibitors for refined gasoline up to 0·05 per cent. by weight; effectiveness was somewhat lower than that of commercial inhibitors. In the reviewer's knowledge this effect of the phenols in cracked distillate is not always the same, for in some cases pre-soda treatment is essential to obtain the best results from the subsequent acid treatment.

Polymerisation as a function of acid concentration temperature and quantity is the subject of an article by Morrell and Egloff.[43] It is shown that acid sludge–acid ratio increases as a straight-line function of the temperature, and also with increase in strength of acid. The ratio decreases somewhat with increasing amounts of acid of the same strength between 5° and 100° F. Increase in acid strength increases solution loss and polymerisation, the former being reduced with lowering of temperature, the reduction being substantially less than the decrease in polymerisation, although this is very marked. In general, treatment of cracked distillates at low temperatures shows an all-round saving in losses. The degree of desulphurisation increases with increase of acid strength, but depends also on the nature of the sulphur compounds and the distillate. Pretreatment with soda has a beneficial effect on desulphurisation. Gum content is decreased with increase in amount and strength of acid, whilst colour improves with increase in amount of acid to a maximum, then falls due to over-treatment; it improves within limits with constant amounts of acid of increasing strength. According to Nikolaeva and Kalitta,[44] cracked distillate from Vickers, Jenkins and Winkler–Koch units in Grozny can be satisfactorily refined by passage through a soda agitator, an acid agitator, then a soda agitator, and then distilled with steam (10 per cent.) in a batch still. Fussteig [45] describes a continuous-treating plant in which two acid agitators are connected by an interposed cooling device. In the first agitator the oil is treated with acid used in the second (well insulated) agitator, in which the gasoline (cooled to 10° C.) is treated with acid cooled to −12° C.; both agitators contain means for mixing oil and acid and for separation of sludge. A general account of the acid treatment of cracked distillates has been given by Critchley,[46, 47, 48] and includes methods of desulphurisation. The laboratory distillation of acid-treated P.D., often troublesome with regard to correlation with plant practice, has been studied by Dailey, Meier and Shaffer,[49] who showed that there was a wide variation in the colour of a cracked distillate treated with varying percentages of acid (0·75–6 lb./brl.), but distilled under different conditions; thus a gasoline

treated with 0·75 lb./brl. and distilled at 0·02 mm. pressure had a final colour superior to that of the same gasoline treated with 6 lbs. acid/brl. and distilled first to 315° F. at atmospheric pressure, then under vacuum at this temperature. The gum test was the same in both cases. A glass lab. still (2 litres/hr. capacity) and an iron still (5–7·5 litres/hr. capacity) were constructed combining atmospheric steam and vacuum, which gave good correlation with the plant over a 48-hour run with regard to operating temperatures, analyses of overhead and bottoms, etc.

Pre-treatment of pressure distillate is described by Crosby and Carney,[50] who suggest treating the oil with a 2–5 per cent. suspension of lime under pressure, then removing the oil-soluble calcium salts of organic acids and some H_2S by treating with a small quantity of 15–30° Bé. soda. Woodward,[51] in discussing the uses of anhydrous ammonia in petroleum refining, indicates that it obviates formation of emulsions in neutralising acid-treated distillates, minimises corrosion in P.D. re-run units, and can be used to neutralise the hydrochloric acid formed in the Lachmann zinc chloride process. The rational refining of cracked gasoline is the subject of an article by Vellinger and Radulesco,[52] who consider that gum formation is frequently greater in refined gasoline than in the unrefined product, and suggest that refining removes certain natural gum inhibitors; their experiments showed that the addition of a small proportion of unrefined gasoline improved the refined product, whilst an examination of the distillate fractions of unrefined gasoline indicated that the inhibiting action was most effective in fractions distilling above 130° C. They suggest that economies in refining could be realised by fractional distillation, then blending of the light and heavy fractions in suitable proportion to give a gasoline of the desired properties. The light fraction could be treated in the ordinary way, whilst the heavy fraction need not be treated, or, if at all, be given a moderate earth treatment. A number of refiners will, no doubt, disagree with these views, and suggest that the light fraction receives a caustic or doctor wash while the heavy fraction is more fully treated, *i.e.* by acid or vapour-phase earth treatment. In the reviewer's opinion, the method of treatment chiefly depends on the composition of the cracked distillate, and the products desired, and each pressure distillate must be investigated to ascertain whether it is more economic to refine as a whole or in fractions.

The treatment of gasoline with hypochlorite, wherein the pressure exerted on the gasoline in the stabiliser is used to circulate the solution with a jet, using the solution until completely spent, is described in an anonymous article.[53] Of general interest in gasoline treating is that *cyclo*hexene reacts with SO_2 in the presence of an oxidising agent such as hydrogen peroxide, yielding a polymeric sulphone.[54]

The number of patents covering various chemical methods of refining cracked distillates does not appear to diminish, and the following may be noted In vapour-phase refining Egloff and Morrell give the use of the following acidic mixtures, aqueous acid [55]; steam, SO_3 and a metal oxide [56]; steam, SO_3 and fuller's earth [57]; steam, oxygen, SO_2 and fuller's earth [58]; oxygen and SO_2 [59]; dilute sulphuric acid and an alkali sulphate [60]; dilute sulphuric acid, air and ferric oxide [61]; a mixture of sulphuric and acetic [62]; or chloroacetic acids [63]; phosphoric acid and an earth [64]; ozone followed by aqueous alkali [65]; a borate solution [66]; hydrochloric acid and zinc chloride

solution [67]; and hypochlorous acid in the presence of a copper or iron salt.[68] For liquid-phase treatment they suggest aqueous sulphuric acid containing calcium sulphate [69]; or sodium hydrogen sulphate.[70] According to Miller and Connolly,[71] cracked distillate may be treated with sulphuric acid sufficient in strength and amount to polymerise the more active gum-forming constituents, then subjected to heat treatment under pressure to polymerise similar bodies that are less reactive. Lewis [72] suggests treatment with dilute acid at 70° F. followed by strong acid at 38° F., then at 70° F., sludge being removed at each stage. The use of certain magnesium compounds for neutralisation of acid-treated distillates has been covered by Caldwell and his associates; thus the acid and soda-washed distillate is vaporised, and with steam passed over MgO,[73] to react and form water-soluble salts, or the acid oil is percolated through opaline [74] or treated with powdered dolomite in the presence of water,[75] or contacted with a granular, water-insoluble material containing magnesium hydroxide solution.[76] According to Dickey,[77] acid-treated gasoline may be neutralised by being heated until decomposition of the sulphonates begins, and then being contacted with solid caustic soda. Connolly and Wurgbacher [78] have patented the use of steam for separation of colloidal sludge from acid-treated oil, the steam condensate bringing down the sludge as it settles.

The use of aluminium chloride for refining cracked distillates appears in two patents; in the one this reagent is used alone,[79] and is supplemented by the action of the silent electric discharge, whilst in the other it is used in the form of a complex with a gaseous olefin; [80] in each case mild treating conditions are employed. The use of hydrochloric acid in refining gasoline appears in a number of patents, which, in addition, involve the use of brass,[81] metals,[82] aluminium and an aldehyde [83] and greensand plus steam.[84]

(c) *Physical Refining.*—Practically the only physical method of refining gasoline that is commercially operated, or has been seriously investigated, is treatment with earth or clay in the vapour and liquid phases. With regard to the Gray process, Cooke and Hayford [40] state that since its inception in 1924 units to the aggregate capacity of over 100,000 brls. have been installed. Losses in normal operation range from 0·5 to 1 per cent. on most stocks at a treating cost of 2 cents/brl. The refined product has a low gum content, good colour and is sufficiently stable to meet competitive marketing requirements. No depreciation in octane rating is incurred. Steininger [85] discusses the general arrangements of clay-treating equipment (vapour-phase) and rates of treating, data being given. He also indicates the gum and oxidation stabilities of clay-refined cracked gasoline, together with the effect of colour stabilisers on it. Using initial colour as criterion, yields of 5000–6000 brls. per ton of clay may be obtained. Increases in pressure, temperature and contact time, improve colour stability, and there is a definite relation between yield and oxidation characteristics of the treated product—the induction period is favourably affected up to a yield of 4000–5000 brls./ton. The use of the Gray process in refining Rumanian cracked distillates is described by Voicu.[86]

The liquid phase clay-treating process as exemplified by the Osterstrom process has been discussed by Cooke and Hayford,[40] who state that it is better adapted than the Gray process to the treatment of gasoline from

cracking units producing a relatively large volume of highly reactive gas (*e.g.* the Gyro process). In the Osterstrom process the distillate flows through a bed of 30–90 mesh fuller's earth at 500–600° F., and thence back to the furnace for a slight addition of heat, so that when the stream passes to the polymer fractionating power vaporisation will occur to such a degree that reflux can be pumped back to assist fractionation. The process has been applied to Gyro distillate, and more than 20,000 brls./day treating capacity have been installed. More than 70,000 brls. gasoline per ton fuller's earth can be obtained, but for colours of 25 plus the yield is lower. The octane rating is practically unaffected.

Mainz and Muhlendyck [87] have studied the action of various bleaching earth in the refining of 97 per cent. crude benzole boiling between 80° and 180° C., and find that floridin and tonsil are the most efficient, but to obtain a highly refined product it is necessary to steam distil after treatment. The following patents on the physical refining of gasoline may be noted :—treatment of the vapours with a finely divided dry adsorptive polymerising earth maintained in suspension by the vapour velocity,[88] contact of the vapours with an earth impregnated with copper oxide,[89] treatment of the vapours with an earth in the first stage, condense and treat the condensate with fresh earth in the liquid phase in the second stage,[90] heat treatment of the vapours at about 650° F. followed by refluxing of the gasoline, the reflux being returned to the heat-treatment stage,[91] and heat treatment in the liquid phase at 1000 lb. pressure at below cracking temperature for 5 minutes.[92]

Kerosine.

A general discussion of the refining of kerosine, with particular reference to acid and Edeleanu treatment, is given in an article by Critchley.[93] According to Clark [94] improved kerosine is produced by hydrogenating unrefined distillates at high temperatures and under 20 atmospheres' pressure at a rate greater than 0·1 volume of oil per volume of reaction space per hour, but quick enough to prevent the formation of more than 20 per cent. of light oil boiling below the kerosine range. In the solvent treatment of kerosine R. K. Stratford [95] has patented the use of a mixture of methyl alcohol and phenol in an amount equal to 65–95 per cent., the extraction temperature being just below that of complete miscibility.

Lubricating Oil.

(a) *Chemical Refining.*—The use of the centrifuge in the acid treatment of lubricating stocks continues to attract attention. Jones [96] considers that early attempts to separate mixtures of sludge and oil were uniformly unsuccessful, continuous discharge of the sludge being prevented by clogging of the centrifugal rotors and suitable equipment for feeding a uniform mixture to the centrifuge was not available. He describes the design and operation of an installation treating 1000 brls./day cylinder stock, and which incorporates special proportionometers for the charging of the required amounts of acid and oil and super-centrifuges for the continuous separation and discharge of sludge and sour oil. The outstanding merit of the centrifuge is the reduction in loss of treated oil to sludge.

The saving in acid consumption may be great or small, according to the nature of the oil treated. According to Walker,[97] of importance equal to that of centrifugal separation has been the development of equipment to effect proper treatment of the oil, and at the same time pass the acid-treated oil to the centrifuge in the optimum condition for separation. He discusses the operating sequence, and indicates that the important factors in control are quantity of acid, treating temperature, degree of mixing, contact time and degree of separation. He describes a bowl centrifuge that discharges three components, sludge-free oil, heavy viscous sludge, and free acid continuously. Tests on different oils showed that this method held the following advantages over the batch method: a saving of 25–50 per cent. in acid requirements, a similar amount in earth or neutralising agents and in treating loss, a more stable oil, a less viscous sludge, and greater operating flexibility. The question of acid sludge is examined in an article by Trescott,[98] who indicates that its character is effected by the oil, the quantity and strength of the acid, the method and time of agitation and the amount of water used in settling. The increase in yield obtained by treating heavy oils in naphtha solution renders consideration of the economic possibility of this method necessary. He gives the flow diagram of a continuous acid and clay-treating plant. The acid treatment of lub. stock from Osage crude is given in an anonymous article.[99] A long residuum is treated with sulphuric acid 35 lb./brl. and the acid-treated stock is neutralised with ammonia. After dilution with its own volume of naphtha, it is filtered through clay at 100° F., then more naphtha is added and it is dewaxed at — 45° F. The naphtha is then distilled off and the remaining oil is distilled with steam to give a bright stock finished by earth percolation. In an article on the use of propane in lub. oil refining, Bray, Swift, and Carr[100] indicate that after asphalt and wax separation acid treatment of the propane-containing oil has been effective for residual oils of the mixed-base type. The sludge separates cleanly, and alkali washing proceeds without tendency towards emulsification.

An informative article by Nugey[101] deals with the production of white oils, the characteristics of the various grades, their uses, and the market needs being discussed. The following process is described. The starting material was a paraffinic distillate of 420 secs. Saybolt viscosity at 100° F., and it gave a 50 per cent. yield of white oil of 250 secs. viscosity. It was first treated with 2 per cent. by volume of 66° Bé. acid to precipitate asphaltic matter, then agitated with cooling, with 50 per cent. of 20 per cent. fuming acid added slowly. The sludge was settled out in two wood settling-tanks, and the oil was neutralised with soda. The sulphonated oil soaps were extracted with methyl alcohol, and the oil was then washed with water and dried by air blowing. It was then mixed with fuller's earth (30–60 mesh plus fines) and filtered on a Sweetland filter. The equipment is described and the working costs are set out. The refining of transformer oil has been examined by Boltus-Goruneanu,[102] who concludes that the best results are obtained by treating, with 20 per cent. of 60 per cent. acid, a suitable cut made by high vacuum distillation. In a general article on the use of anhydrous ammonia in refining, Brooks[103] states that this reagent can be used with advantage in place of soda to neutralise the acid oil in white oil manufacture, since it has little tendency to form emulsions.

Procedures for the avoidance and breaking of emulsions in acid treating are given in an anonymous article.[104]

The following patents with regard to the chemical refining of lub. oil may be noted: refining the oil with acid followed by washing with a water-soluble sulphonic acid, and finally contacting with clay at an elevated temperature;[105] refining lub. oil with 8–10 per cent. chlorosulphonic acid, then neutralising by admixture with an adsorbent at 250–300° F.;[106] treatment with not less than 20 per cent. by weight alkali metal[107] or alkali metal–polymer compound[108] at a temperature above its melting point; reaction products and metal are filtered from the refined oil—by treatment of a propane deasphaltised oil with $AlCl_3$[109] at a temperature below cracking temperature and by treatment with acid followed by neutralisation by percolation through a bed of wet magnesium oxide-containing mineral.[110]

(b) *Physical Refining.*—(i) *Adsorption.* Travers[111] and Eckart[112] have studied the activation of bleaching earths. The former considers that activation by dilute acid treatment is due to a large extent to the liberation of free SiO_2 which acts as a gel; earths not attacked by acid cannot be activated, but if they are rendered permutitic by alkali treatment they can be subsequently activated. The latter states that activation may be carried out by treatment with 10 per cent. HCl, but traces of iron and aluminium chlorides remain in the earth; he suggests that decomposition of aluminium oxide causes enlargement of the surface. According to Delemar,[113] the activity of a bleaching earth varies with the conditions of its use, it bears no simple relation to the rate of filtration of the oil, to the ease of wetting by the oil, or to the amount of heat evolved. He suggests methods of evaluation, and regards activation as due to the formation of a special form of SiO_2. Shepard[114] has communicated an informative article on a specific gravity system for the maintenance of quality of fuller's earth. He states that the common cause of the lowering of decolorising power of clays after each burning is the incipient fusion which occurs, and discusses the advantages obtained by use of a concentrating table operating on an air flotation principle. This machine removes the denser inert material produced by burning, and it is shown that its application led to an earth after the tenth reburning having the same decolorising quality as, in the absence of re-processing, would attach to the earth after the second burning.

Filter-cake problems are the subject of three articles by Trescott. In the first[115] the handling of filter cakes from cylinder oil–naphtha solutions and light oils is discussed. The filter cake from naphtha solutions is either steamed dry, or blown with air or inert gas. Steaming is the simplest, but cannot be applied to clay from treating sour oil, whereas air blowing carries fire risks. An alternative is to sluice away the spent cake with a high-pressure stream of naphtha and thicken the outcoming slurry in a "sock" type thickener discharging the slurry (contains 50 per cent. naphtha) to a vacuum drier, which strips the cake to less than 1 per cent. solvent. Cakes from lighter oil filtration are either air blown, if from a pressure filter, or not treated in any way, if from a vacuum filter. The second and third articles[116] deal with the solvent reactivation of spent contact filter cake. A review of the literature of solvent reactivators is given, and it is indicated that, from the point of view of cost, benzole, solvent naphtha, alcohol and its associated compounds only need be considered. Some agents, *e.g.* alcohol, acetone,

are suitable for all cakes, while water–alkaline solutions and soap solutions may be used in some cases. When alcohol or acetone is used with benzole, 10–15 per cent. by vol. is used; the alcohol must be completely miscible and be there in sufficient proportion to prevent emulsification, made possible owing to the presence of moisture in the cake. When benzole or naphtha is used as a solvent, water may be added in small batches at regular intervals. Extraction of oil from the clay is a relatively short time process, but reactivation generally takes longer, being usually performed at 160–170° F.; the clay is finally vacuum dried. Extractors used in clay recovery work on the Soxhlet principle with means for agitation. The total costs per ton of spent cake reactivated using naphtha–water, naphtha–alcohol and benzole–alcohol are estimated at \$4.27, \$5.05 and \$6.87 respectively, against which has to be offset the value of the tar and oil recovered.

Funsten [117] gives an analysis of a system of costing oil percolation filtration methods to evaluate the degree to which various refinements influence the final cost of the products—the cost items of filtering a cylinder stock both alone and in solution include labour, steam for washing, naphtha loss, filter washing and fuel–clay burning. The effect of time and recycling on the composition of a product after filtering has been mathematically formulated by Khokhryakov,[118] and applied to laboratory batch work, enabling the preparation of a product similar to that obtained in a large-scale continuous contacting plant.

(ii) *Solvent Extraction.* The interest taken in refining methods that come under this title was maintained during 1934, and it is reasonably safe to forecast that during the next year or two refining zones outside U.S.A. will be operating treating plants using solvents other than liquid SO_2, which of course has been in international use for some years. Wilson and Keith [119] discuss the economic aspects of solvent refining, and taking low carbon formation, low pour point, high viscosity index and resistance to oxidation as the most important characteristics of a motor-oil solvent extraction facilitates production of such oils from a wide variety of crudes. Comparing the single and double solvent processes, the former are more adapted to distillates, the latter to residues. In the latter the precipitation of asphalt by propane results in better-coloured oils from residual stocks, although propane de-asphalting followed by a single solvent gives similar results. Neither type of process requires acid treating, but in general both require dewaxing and clay treatment. Data are presented on solvent dewaxing and extraction plants in operation and under construction in U.S.A. The solvent refining of lubs. from Mid-Continent crudes gain some advantage in that more crude is run than is processed for lubricants, so the yield of refined products is important only in so far as it affects plant costs. This consideration operates as a disadvantage with Penna crude, dependent on its value for its lub. production, so loss of yield is important. The production of oils of high viscosity index from asphalt-base crudes is considered not economically justifiable, but extraction will be employed to produce ordinary industrial lubricants. According to Albright,[120] solvent refining methods are being carefully studied by Mid-Continent refiners to determine the most satisfactory solvent to employ. So far only one refiner has made a selection, *i.e.* Chlorex, for the following reasons: (1) Solvent loss is exceedingly low; (2) easily separated from the respective fractions; (3)

capable of effecting a sharp separation between paraffinic and naphthenic layers; (4) of such solvent power that reasonable amounts are used to give the desired results; (5) non-reactive with stocks under process conditions; (6) practically insoluble in water and (7) low vapour pressure; handling hazards are small and it is no more toxic than gasoline. The complex patent situation is advanced as a reason for deterring these refiners from choosing a suitable solvent. R. K. Stratford [121] discusses the above reasons for the selection of chlorex and, comparing it with phenol, nitrobenzene and furfural, indicates that they are not sufficient to prove that this solvent is superior to the others. Foster [122] states that in the U.S.A. four companies are operating the Edeleanu process, one the phenol process and two the chlorex process, while units known to be under construction or contract are: one each using propane, furfural, nitrobenzene and acetone–benzole and three using the Duo Sol process. The same writer [123] later states that for the year ending Oct. 1st, 1934, 1,000,000 brls. of lubricants had been solvent extracted.

The operation of various solvent units has been the subject of a number of communications. Stockman [124] describes the solvent extraction unit at Oleum, California. Propane de-asphaltised and dewaxed oil is extracted under pressure with benzole–SO_2 and vacuum distilled; 1200 brls. of finished lub. oil daily are produced, and including de-asphaltisation and dewaxing the stock passes through twelve stages. Foster [125] gives an account of the 3000-brl. Duo-Sol unit installed by the Vacuum Oil Co. at Paulsboro, N.J. It consists of three sections: the extraction unit, the recovery stills for recovering the paraffinic solvent, *e.g.* propane, from the refined oil and the stills for removing the selective solvent, *e.g.* cresol, from the extract. The extraction unit is composed of nine mixing–settling stages arranged so that each portion of incoming stock is freed of undesirable constituents and the raffinate and extract are concentrated in their own particular solvent. A flow sheet of the process is given, and data are presented on the processing of a variety of residual stocks, which indicate that the yield of refined oil (not dewaxed) with a V.G.C. of around 0·800 may vary from 80 to 56 per cent. N. Williams [126] describes the Duo Sol unit erected at Beaumont, Texas, by the Magnolia Petroleum Co. This is a 2000-brl. unit operating on Oklahoma residuum. The propane used is approximately 325 per cent. of the charge, while the proportion of cresol or Selecto solvent is about 380 per cent. The latter solvent is Selecto No. 2, being a mixture of cresylic or tar acids with 35 per cent. phenol. The yield of refined oil of V.G.C. 0·800 is 76 per cent.; dewaxing of this oil is carried out by the Sharples process.

A number of general articles on the different solvents have been communicated during the year, *e.g.* chlorex,[127] phenol,[128] nitrobenzene [129] and various solvents.[130]

Waterman and others [131] have studied the course of the treatment of oils with liquid SO_2 by means of specific refraction and aniline point, and conclude that differences between raffinate and extract can be ascribed to the higher percentage of aromatic rings in the extract, although the average number of rings per molecule is about the same for each product. Fenske [132] states that the effect of eighty different solvents are being investigated with regard to their action on Penna neutral oil and bright stock, but the

research has not yet reached the stage where comparisons can be made. Two Polish articles deal with the use of paraffin gases [133] and cresol [134] as selective solvents respectively, while Calantar [135] describes the use of Edeleanu treatment to produce transformer oils from Russian crudes.

The following solvents have been patented during the year: nitrobenzene for white oil [136] and transformer oil [137] production, phenol and methyl alcohol,[95] phenols from cracked distillate,[138] liquid SO_2 followed by distillation over alkali,[139] liquid SO_2 under pressure at 85° F.,[140] acid, liquid SO_2 and benzole,[141] chlorex and liquid SO_2,[142] chlorex and acetone,[143] tetrahydrofurfural,[144] 3 furfural,[145] furfural in amylamine,[146] furfuraldoxime,[147] liquid trimethylene,[148] crotonaldehyde,[149] and nitriles or organic thiocyanates.[150]

(iii) *Dewaxing.*—Progress and interest in this phase of lub. oil refining have been maintained during the year. Solvent dewaxing and solvent extraction are more or less interdependent, and it is doubtful whether the latter would have made such satisfactory progress had dewaxing methods not shown similar developments.

The use of propane for dewaxing is described in communications by Bray, Swift and Carr [150] and Conine [151] (paper by P. C. Keith). The former describes researches carried out by the Union Oil Co. of California—in dewaxing refrigeration to about − 40° F. is obtained by releasing the vapour at a controlled rate corresponding to a fall of 2° to a 3° F. per minute. The low viscosity of the chilled mixture in combination with the physical structure of the wax ensures ready filtration with lub. distillates, whilst the low sp. gr. and viscosity of liquid propane facilitates cold settling in the case of heavy residual oils. The latter describes dewaxing a typical Penna long residuum (74 secs. S.U. at 210° F.) by diluting with propane, cooling to − 40° F. by evaporation and continuously removing the wax on a rotary filter. The yield of dewaxed oil was 80·6 per cent. of pour point − 12° F. (reduced from 70° F.), whilst viscosity and Conradson carbon value remained practically unchanged. This indicated removal of asphaltic matter which was confirmed by a 50 per cent. increase in filter yield. By treatment with varying propane concentrations and by varying the temperature between 120° F. and 160° F. in four stages, a Penna residuum (172 seconds S.U. at 210° F.) was fractionated into 8·2 per cent. resins of high viscosity, 72·3 per cent. light blending stock (121 seconds S.U. at 210° F.) and 17·3 per cent. cylinder stock (235 seconds).

In a paper on oiliness of lubricants, Wardner [152] describes the extraction with acetone of an insoluble residue from Penna residuum which he considers is responsible for oiliness. According to consistometer data, normal dewaxing does not extract this material, but excessive dewaxing removes it, with subsequent decrease in quality. According to Katz,[134] residual oils and distillates from the vacuum distillation of Boryslaw crude can be dewaxed by using naphthalene, the latter crystallising out on cooling, forming a spongy mass with the wax which can be filtered.

The use of trichlorethylene as a dewaxing solvent has been put into commercial operation at the Port-Jerome refinery in France.[153] This dewaxing unit employs six De Laval S–N centrifugal separators giving an output of 500–630 brls. dewaxed oil per day. The proportions of oil and solvent vary around 54 and 46 respectively, the dewaxing being carried out at about

– 13° F. The pour points of the motor oils produced are of the order of – 6° to — 12° F. The wax, although of crystalline structure, discharges easily and continuously from the bowl. With regard to the centrifugal dewaxing of long residuum and bright stock, Hodus [154] gives a method of determining the oil losses due to retention by the separated petrolatum.

Patents in connexion with methods of dewaxing may be listed as follows.

Benzole–acetone : addition of these solvents in equal proportions to oil–wax mixtures, cooling to — 5° F. and filtering under pressure to separate a sweatable wax and a lub. oil of zero pour point [155, 156, 157]; addition of 1 part acetone and 2 parts benzole, cooling to 0° F. and filtering through a diatomaceous earth,[158] and addition of this solvent mixture to an oil–wax mixture cooling to — 5° F. and removing relatively high melting wax in a filter press, then cooling to — 23° F. and removing low-melting wax.[159] Nitrobenzene [160] wax is concentrated in the raffinate and removed by chilling and settling; dichloromethane [161]—cooling to 0° F. and filtering; butane and butane–propane mixtures [162, 163, 164]; *iso*propyl ether and acetone (60 : 40 by vol.) [165]; gaseous alkyl and alkylene ethers under pressure with evaporative cooling; [166] a blend of 60 per cent. amylene dichloride and 40 per cent. methyl ethyl ketone, cooling to — 10° F.; [167] a mixture of equal amounts of benzole and methyl acetate with cooling to — 15° to – 50° F.[168] and synthetic alcohols of boiling range 290–410° F. used at ordinary temperatures.[169]

A novel method of separating wax from oil has been patented by Stanton.[170] Electric charges of a definite polarity are impressed on the wax particles by subjecting the wax-bearing oil to the action of a high potential unidirectional current, and the charged particles are collected on an electrode of opposite polarity with which the wax-bearing oil is brought in contact.

Paraffin Wax.

It is a curious fact that, as far as published literature is concerned, there appears to be little progress in the development of the methods of production and refining of grades of paraffin wax suitable for specific purposes, although this material, in general, commands a relatively high price. The year under review is no exception to previous post-war years. Fussteig [171] discusses the manufacture of paraffin, and states that isomeric paraffin compounds impart variable properties to oil–wax mixture in relation to solubility, crystallisation and ease of filtration. In separation of wax from oil by filter-press methods solvents may be added which favour the formation of needles instead of plates. Filter cakes 16 and 26 mm. in thickness indicate that the thicker the cake the less oil it contains after pressing. Paraffin may be decolorised by warming to 80–110° C. with bleaching earths, but the author prefers the method of refluxing the paraffin in solution through a tower containing an adsorbent earth. Better sweating of paraffin is obtained if it is carried out in jacketed cylinders. Paraffin may be purified by treatment with acid or phenol, the latter being preferred. The same author [172] also discusses the recovery of adsorbed wax from earth used in refining paraffin. Biluchowski and Dobrowolski [173] have shown that ferric sulphate can replace sulphuric acid in paraffin refining, and state that an odourless paraffin can be obtained; the use of this reagent on a large

scale is not possible owing to its high price. A short account of the production of paraffin is given in a new book by Ivanovskii [174] on ozokerite and allied substances.

Patents relating to the refining of paraffin may be given as follows: refining crude wax by hydrogenation in the presence of a catalyst consisting of oxides and sulphides of metals of group six of the periodic system [175]; treatment with 20 per cent. by weight, chlorosulphonic acid [176]; and washing the crude paraffin with a mixture of methyl formate and benzole-methanol to remove oily and asphaltic substances.[177]

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THEORY OF DESIGN OF DISTILLATION EQUIPMENT.

By P. Docksey (Associate Member).

This review of publications during the past year dealing with the theory of design of distillation equipment, or which are useful in that connection, is divided into three sections—

(1) *Design of Columns*, including the calculation of compositions in fractionating columns for complex mixtures, determination of plate efficiency, effect of entrainment, etc.
(2) *Heat Transfer* to fluids in pipes, in heat exchangers, condensers and evaporators.
(3) *General*. Papers dealing with the film concept and diffusion, and with laboratory apparatus.

Design of Columns.

The methods proposed for calculating compositions in various parts of a fractionating column for complex mixtures may be divided into two classes. First, there are those in which equations based on some theoretical conception of the action of the column are derived for the change in composition. Granted the initial assumption which has to be made, the equations produced are exact: they contain no approximation, and so are particularly useful for the purpose of analysing data from experiments on fractionating columns in order to prove whether the initial assumption was or was not correct. It is found, however, that these exact equations are exceedingly troublesome to apply to design, and for this reason there have been many methods of the second class proposed, in which some approximation is introduced either into the equations or into the method of using them, which will allow them to be applied to design with reasonable convenience. Examples of both methods have appeared during the course of the year.

Underwood [1] gives equations from which the plate efficiency for any component in a complex mixture may be determined if the compositions of the liquid on adjacent plates are determined. Three cases are discussed: the conventional cases with and without steam, and also the case of distillation with saturated steam, *i.e.* when the partial pressure and temperature conditions are such that water exists in the column. The last case is not a common one in practice, but was found to occur in the column of a continuous still used for white spirit distillation, a very complete test on which is described by Goodliffe.[2] The 22-plate column was arranged so that samples of liquid could be withdrawn from all trays for analysis. A complete heat balance is presented in detail, and true boiling-point analyses of the products from the still, and of the liquid samples from fifteen plates, are tabulated. The relation between molecular weight and specific gravity, and between boiling point and deviation from Raoult's Law were determined for the material composing the feed to the still. Using this information,

individual plate efficiencies were worked out for various components by means of the equations developed by Underwood, and were found to vary widely. The over-all plate efficiency found by the application of Underwood's method was 16 per cent. This figure is very low, and the author gives as an explanation the fact that many plates were working below the minimum reflux ratio as indicated by Underwood's equation. It should be noted that this equation applies only to a theoretical plate, so that its use in this case is of doubtful validity. A probable reason for the low overall plate efficiency is the effect of the water on the trays.

G. G. Brown and his co-workers have published several papers [3, 4, 5] devoted to a method suitable for design of columns—namely, the "Absorption Factor Method." The various disadvantages from which the published methods suffer when used for design purposes are discussed, and the theory of the absorption factor method is fully explained.[3]

This method depends on the assumption that the correct result is obtained if an average equilibrium constant is assumed for any particular component and used for calculating the enrichment throughout any section of the column. The average value is taken as the arithmetical mean of the values of the equilibrium constant at the top and bottom of the section of the column under consideration. In order to apply the method, it is necessary to know the composition on the feed plate and the temperature of this plate and at the top and bottom of the column. These are calculated by methods which have previously been suggested (*e.g.* Underwood). The equation used for obtaining the composition on the feed plate can be applied only to the case of a correctly designed column (*i.e.* one in which the number of plates in the stripping and rectifying columns are in the correct ratio). This imposes a limitation on the method, which occurs, however, in several other proposed methods of design. It would appear that the assumption made as to the applicability of an average value for the equilibrium constant is not likely to lead to trouble at low reflux ratios, but it may not prove to be accurate when the temperature difference between top and bottom of a column is large.

It is pointed out that whether the Absorption Factor method is trustworthy or not can be decided only by comparing calculations made by it with figures obtained by exact methods.

In the second paper [4] the results of six calculations are given which show that the number of plates required for a given separation of a mixture of propane, butane and pentane, may be determined with reasonable accuracy by the Absorption Factor method. The method is compared with the figures published by Underwood for a five-component mixture, and was found to be trustworthy for this case also. The reflux ratio and total pressure were 9 : 1 and 200 lb./sq. in. in the first calculations, and 3 : 1 and 1 atmosphere in the example calculated by Underwood. The six cases for the three-component mixture have been calculated assuming the feed to be introduced at various positions, and the effect of feed plate position on the separation obtained is to be noted. It is assumed in making the calculation that the feed is introduced as liquid at the temperature of the feed plate, but it is observable that in only two out of the six cases could this actually be done; in the other four cases the feed-plate temperature is above the initial vaporisation temperature of the feed at the column

pressure. In these four cases, therefore, the reflux ratios used in making the calculations are not quite correct, but, since the reflux ratio is high, the effect of any small error in it will be negligible.

The third paper [5] described a test on a forty-eight-plate commercial gasoline stabiliser. Samples were taken from seventeen plates and analysed, and compositions on intermediate plates were obtained by interpolation. The plate efficiency was found to be 100 per cent. both by heat and material balance, and by the Absorption Factor method. This estimate was obtained using equilibrium constants uncorrected for deviation from the laws of ideal solution. If corrections are applied, the values for the plate efficiency are erratic, but are all lower than the figure given above.

Meyer [6] has described a method of calculating the composition of vapour and liquid obtained when a complex mixture is evaporated under equilibrium flash conditions. The method has the great merit that molecular weights need not be known. It may also be applied to the case of simple batch distillation.

The paper on overlap coefficients by Meyer [7] has been criticised in two interesting contributions.[8, 9] Roelfsema [8] deals with the question of the desirability of correlating columns by means of the true boiling-point curve or of functions such as overlap coefficient, and concludes that it would be best to correlate column performance by means of such tests as gap between F.B.P. and I.B.P. on the Engler distillations of two products. Both Roelfsema and Cutting [9] criticise the method by which the overlap curves at other reflux ratios than infinite are derived; Cutting illustrates the case by means of figures for an eleven-plate column calculated by Thiele and Geddes' method. He also takes exception to Meyer's statement that "The more plates a column has, the higher is the reflux ratio necessary to make full use of them." In reply, Meyer suggests that if a comparison is made between the figures calculated for a ten-plate column and a twenty-plate column at a low reflux ratio (*e.g.* $\frac{1}{2}$: 1) it will be found that the extra plates decrease the overlap to only a very slight extent.

The effect of the variation of the physical conditions at a bubble plate on the efficiency has been the subject of an investigation by Carey, Griswold, Lewis and McAdams.[10] Experiments were carried out using benzene–toluene and water–ethanol mixtures in three columns. The slot width, height of the overflow weir, and vapour velocity were all varied. The height of the overflow weir was the only one of these variables to have a large effect, the plate efficiency varying from 55 to 99·75 per cent. in the tests made. It was found that a straight line is obtained if weir height is plotted against log $(1 - E)$ where E is the plate efficiency.

Ashraf, Cubbage and Huntington [11] observed the action of a bubble cap in the course of an investigation on entrainment. They suggest that at high rates of flow there is a jetting action due to the caps which greatly increases entrainment. Experiments were carried out using kerosine and dry natural gas as the fluids, and the effects of pressure, velocity and plate spacing were studied. Holbrook and Baker [12] carried out experiments using steam and brine, and examined the effect of velocity, plate spacing, amount of reflux, slot shape and surface tension of the liquid.

Strang [13] made similar experiments using air and water in a single-plate column. The effect on the entrainment of various prevention devices is

recorded, and one in particular appears to be very efficient. A great deal of the entrained liquid from a plate is caught on the underside of the plate above, and is removed from the vapour. A large proportion of this, however, returns to the vapour because the liquid tends to run to the edges of the vapour uptake pipes and drops of liquid are swept into the vapour stream. The successful device consists of extending the vapour-uptake pipes down below the plate, cutting them off at an angle, and attaching a metal strip which hangs downwards and dips into the surface of the liquid on the plate below. The liquid drops, instead of hanging on the edge of the uptake and being caught up in the stream of vapour, are able to flow down the strip.

Measurements of pressure drop through a slot in a bubble cap were made by Rogers and Thiele,[14] and compared with a theory based on the assumption that the slot acts as an orifice. The results show fair agreement with theory.

Heat Transfer.

Fallah [15] gives a general review of the method of calculation of film conductance in turbulent flow. His paper includes charts for evaluating the various terms in the Nusselt equation, for estimating log. mean temperature difference, and choosing the most economical size of pipe. Useful nomograms are also described by Voorhis.[16]

It is customary to apply log. mean temperature differences to multipass heat exchangers, although doing so may lead to considerable error. Underwood [17] has developed formulæ giving the correct mean temperature difference for multipass exchangers, and shows that in a typical case the use of log. mean temperatures may lead to an error of 40 per cent.

It is well known that the heat transfer coefficients between a turbulent liquid and a solid wall are different when the fluid is being heated from when it is being cooled, other conditions (*i.e.* mass velocity and temperature drop across the film) being the same. Kaye and Furnas [18] were struck by the fact that in the case of a gas the effect obtained was in the opposite direction to that occurring with a liquid. The deduction to be made is that there is a factor missing from the Nusselt equation of a type which increases with temperature in the case of gases, and decreases for liquids. The property of viscosity suggests itself, and the authors find that the published data for heating and cooling liquids and gases may be successfully correlated by introducing such a factor. The ratio between the cooling and heating coefficients in two cases in which the temperature fall across the film is the same is given by :—

$$\frac{h_c}{h_h} = \left(\frac{\eta_h}{\eta_c}\right)^r$$

where h_c and h_h are the heat transfer coefficients under conditions of cooling and heating the fluid.

η_h and η_c are the viscosities of the fluid at the main body temperature.

$r = 0{\cdot}5$ for liquids and $1{\cdot}0$ for gases.

This relationship holds for the calculated heat transfer coefficients in the two cases (*i.e.* heating and cooling) when these are correlated according

to a Nusselt type formula using mean film properties, which the authors regard as more logical than using those at the main body temperature. The method of correlation is shown to be successful by means of examples based on figures reported in the literature.

The design of the radiant section of a pipe still is dealt with by McCulloch.[19] In addition to the calculation of coil area, exit flue gas temperature, etc., the heat distribution in a double-row radiant heater is discussed. General discussions of heat transfer are given by Hottel [20] (radiation) and McAdams, Wilkes, and Generaux.[21]

Heat exchangers are always subject to a certain amount of fouling after they have been in service for some time. The resistance to heat flow of films of deposit may be much greater than the calculated film resistance, and it is essential to make allowance for it when designing. The materials causing fouling may be divided into those giving hard, porous, or loose deposits. The thermal conductivities of such materials are discussed by Nelson,[22] who also gives the fouling factors to be expected in plant service. The deposition of coke in pipe still tubes, and the fouling caused by hard water and wax are also discussed. Sieder [23] proposes to introduce a factor of safety to allow for fouling, which is taken to be 1000 times the thickness of the dirt layer divided by the conductivity. It is shown that it is bad practice to increase the area as calculated for the clean heat exchanger by a definite percentage in order to allow for fouling. The effect of deposit in several practical cases is used to illustrate the variation in the fouling factor with time.

The calculation of heat transfer coefficients in a vertical tube condenser involves a knowledge of the thickness of the layer of condensate on the wall and the type of motion. Kirkbride [24] describes experiments to measure the former under conditions of isothermal flow. Four hydrocarbon oils and water were studied. It was not possible to determine the critical value of the Reynolds criterion from these experiments, but a correlation of heat transfer data for diphenyl, gasoline and steam, suggests that for values of the Reynolds number below 2500 the heat transfer coefficient may be calculated from Nusselt's equation, which assumes that the flow is viscous. The results obtained when the liquid flow is turbulent may be correlated by means of dimensionless groups derived from Nusselt's equation. Cooper, Drew and McAdams [25] review the results of six observers on the isothermal flow of water, dilute sulphuric acid and hydrocarbon oil down smooth vertical walls, and conclude that the flow is stream-line for values of the Reynolds number below 2100.

From a consideration of the two papers just mentioned, Colburn [26] has developed equations from which the necessary condenser area can be calculated when a portion of the condensate layer is in turbulent motion. The proposed equations are represented graphically. Since the flow of vapour, which is neglected in the equations, may be expected to increase the heat transfer coefficient, the equations make possible a conservative estimate of the heat transfer surface. It should be noted that these equations cannot be used when dropwise condensation occurs, but the evidence indicates that film forming condensation is predominant with organic materials.

Colburn and Hougen [27] outline a method for calculating the surface

required in a cooler-condenser for condensing mixtures of vapour with non-condensing gases, which takes into account the change in overall heat transfer coefficient along the condenser, and also the fact that the change in heat content of the mixture is not proportional to the change in temperature.

Logan, Fragen and Badger [28] point out that there is very little data available from which heat transfer coefficients may be calculated for the case of a liquid evaporating in a tube. They carried out tests on a vertical tube forced-circulation evaporator using sugar solutions as the fluid, and found that the results may be correlated by an equation similar to that normally used for calculating the heat transfer coefficient to a fluid inside a pipe. The proportion of vapour to liquid was low in these tests, and hence it is not possible to say whether the equation proposed could be applied to pipe still design.

The effects of tube diameter, spacing, etc., on the pressure drop around tubes in a shell type heat exchanger were determined by Short and Stack.[29] From their experimental data relations were determined for the average velocity of the fluid flowing around the tubes in the shell, and for the equivalent diameters of the passage of flow.

General.

No review of the theory of distillation design would be complete without a brief reference to the papers which have appeared during the past year devoted to the film concept, and to diffusion of material through the film. They represent the beginning of an attempt to derive a more fundamental picture of the action which takes place in a plant, whether in a fractionating column where material is being transferred through films, or in heaters or condensers where heat is being transferred. Chilton and Colburn [30] treat the diffusion of material by analogy with the diffusion of heat. Monrad [31] deals generally with the application of the film concept in refining, including heat transfer, distillation, thermal decomposition and evaporation. Sherwood and Gilliland [32, 33] carried out a large number of experiments on evaporation of liquids flowing down a wetted wall column, and also deal generally with the flow of vapours through gas films. As a result of theoretical investigation they conclude that in gas absorption it is better to use an absorption coefficient rather than to express results in terms of theoretical plates, the former being a less involved variable than the latter.

Useful papers on laboratory distillation equipment are those of Fenske, Tonberg and Quiggle [34, 35] (who describe a variety of small-column packings and also two complete laboratory stills), Schicktanz [36] (sintered glass plate column) and Brückner.[37] Mizuta [38] gives a description of an improved form of Othmer still for the equilibrium distillation of oils.

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(The figures in parentheses at end of references refer to I.P.T. Abstract Numbers for 1934.)

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CRACKING.

By Gustav Egloff, Ph.D., M.A. (Member), and Emma E. Crandal.

I. Introduction.

The tendency is still in the direction of higher compression ratios in passenger cars, with the consequence that gasoline of higher octane number will be called for. The average compression ratio of 18 of the leading 1934 cars was 5·83 : 1; and for the same cars for 1935 was 5·99 : 1.[1] Chatfield[2] found a rise in all cars from 5·76 : 1 for 1934 to 6 : 1 for 1935. A new engine head constructed of an alloy of copper is designed to operate at a compression ratio of 8 : 1. The average octane number of regular-grade gasolines sold in the Eastern area of the United States in 1934 is estimated at 69–70; for 1935 it may be expected to be 70–71, with the average for the premium fuels standing at about 76, which is about 2 per cent. of the total gasoline being marketed, and straight-run gasoline (sold as third grade) has an average octane number of 55.

About 10 per cent. of all straight-run gasoline produced in the United States in the year under review was reformed or cracked into high octane gasoline. The relation of cracking to the permissible increase in compression ratio is obvious from comparing analyses of Mid-Continent, Texas, Pennsylvania, California, and Kentucky straight-run gasolines with the cracked gasolines from the same crude oils. The average paraffin–hydrocarbon content of the gasolines was reduced from 74 to 46 per cent., and octane number was raised from 57 to 72.[3] A distinctive property of cracked gasolines brought out by Brown and Singer[4] is that they continue to develop power in the motor after knocking begins, contrasting with both straight-run and "doped" or "leaded" fuels of the same octane number. The investigation of Hubner and Murphy led similarly to the conclusion that cracked gasolines yield more power for the same octane value than tetraethyl lead (leaded fuels?).[5] This is due to the difference in chemical composition of the hydrocarbons present in the gasolines.

The terms "liquid-vapour phase" and "vapour phase" cracking are used in this report with no thought that they are strictly accurate terms describing cracking operations, but rather as a convenient basis for rough classification.

II. Status of Cracking.

The Bureau of Mines gives the preliminary production of straight-run gasoline for the year 1934 as 206,486,000 brl., a gain of 11 million brl. over the year 1933. The cracked-gasoline production during 1934 was 182,433,000 brl., and for 1933 the volume was 180,623,000—a gain of 2 million brl. The totals for straight-run, cracked, and natural gasoline and the motor benzole are as given:

Motor Fuel Produce from January to December in Thousands of Barrels, 42 gal. per brl.

	1934.	1933.	Per cent. Increase.
Straight-run gasoline	206,486	195,622	5·55
Cracked gasoline (losses deducted) .	182,433	180,623	1·00
Natural gasoline	36,217	33,810	7·10
Benzole	1,600	1,368	16·96

The use of anti-oxidants as inhibitors of gum formation made extended gains in 1934, and less and less sulphuric acid and clay treating is being practised. This has meant important savings to refiners, in one case amounting to 17 per cent. per brl. of gasoline. More than 75 per cent. of all gasoline now marketed in the United States is dyed, again a simplification of the refiner's task. The gasoline sold, particularly in California, Oregon, Washington, Idaho, Nevada and part of Texas, is estimated to contain an average of 0·25 per cent. of sulphur, and in some localities it rises above 0·4 per cent.

The petroleum chemical industry has developed to utilise profitably the by-products of cracking in the form of olefinic gases. The Carbide and Carbon Chemicals Corporation has just completed a $10,000,000 plant at Whiting, Indiana, to synthesise alcohols, glycols, alcohol ethers, ether oxides, aldehydes, ketones, esters, acids, aldehydes, chlorinated compounds, amines and vinylite resins. This plant is an extension of one in West Virginia which has been in operation for a number of years.

Interest in Diesel fuels, both straight-run and cracked, is becoming keen, as indicated by Rendel,[5a] chairman of the Volunteer Group for Compression Ignition Fuel Research, Diesel Fuel Testing Committee, who is the authority for the statement that a properly designed high-speed Diesel will operate smoothly at all loads and speeds on oils of 40–45 cetene number and that American Diesel fuels range from 75 to 33 cetene number, gas oils from cracking between 55 and 33. In the opinion of Hubner and Murphy,[6] the better the Diesel engine can be adapted to run on a cheap readily available fuel like pressure distillate bottoms or other secondary products of cracking, the faster will its adoption spread. A refiner in California whose company has been co-operating with some of the Western railroads in railcar development discovered that a single "uncracked cut" in his overhead cracked products had a high cetene number and was suitable railcar Diesel fuel. He now makes a point of finding this special cut and distilling it out.[7]

III. Economics of Cracking.

Cracking introduces a competitive factor in the motor-fuel industry and into the gas, coal, fuel oil, synthetic resins, alcohol, asphalt and coke industries.[8] Cracked gases have an average heat content of about 1,400 B.Th.U. per cu. ft., some 300 B.Th.U. higher than natural gas. Hence they are useful for blending to raise the heating value of other gas, or they may be reformed to lower B.Th.U. gas. The speed with which liquefied propane and butane, derived from natural gas and the cracking process, have made a place for themselves in the fuel market is due to the ease with which

the gases are liquefied, their high heat value of 2,550 and 3,200 B.Th.U., respectively, and the ready transportability of the liquids in cylinders, tanks or pipe-lines. Localities beyond the reach of gas mains and electric lines can be supplied by them with light and heat. In certain towns liquefied gas has even displaced the gas-making plant. Cracked residual fuel oils are superior to the straight-run fuel-oil residuals in viscosity, have about 10 per cent. more heating value on a volume basis, and give a lower cold test. The properties of fuel oil produced by cracking are subject to control as a function of cracking conditions. The ground lost by the coal industry to cracked fuels in 1932 figures out on the basis of heating value at 19·7 per cent.

IV. Cracking outside the United States.

A number of the French refineries are now receiving crude oil from Iraq. The Iraq petroleum yields about 27 per cent. of straight-run gasoline, which has a low octane number and must be reformed. The Cie Française de Raffinage is adding a reforming plant to its cracking equipment at the Le Havre refinery, and the new refinery at Martigues will be similarly equipped. La Société Anonyme des Pétroles Jupiter is installing a Dubbs cracking unit at its Petit Couronne refinery at Rouen.[9]

The Iraq reduced crude from which 26·8 per cent. of 395° F. end-point gasoline has been removed was cracked to yield between 40 and 45 per cent. of 67-octane-number 380° F. end-point gasoline.[10] One of the representative Iranian crude oils was topped and cracked in a pilot plant operating on the principles of a Dubbs cracking unit. The straight-run gasoline, the reformed naphtha, and the cracked gasoline from the topped crude oil made a total of 61·3 per cent. of 70-octane-number gasoline. To secure a 75-octane-number gasoline from the naphtha, a once-through cracking operation was adopted. The topped crude was cracked by the "two-coil" system.[11]

The U.S.S.R. now operates thirty-six cracking units, with an annual charging capacity of 5,580,000 tons per year. Reforming is being undertaken, straight distillation will sometimes be combined with cracking to utilise the waste heat of cracking, and it is planned to convert cracked fuel oil to asphalt with the aid of vacuum steam towers.[12]

In its refinery at Talara, Peru, the International Petroleum Co., Ltd., operates tube and tank-cracking stills. Light distillate, Diesel oils, bunker fuel oil and a very little coke are produced.[13]

V. The Cracking Reaction.

In "Physical Factors Governing Cracking Operations," [14] a contribution to a symposium on hydrocarbon decomposition conducted by the American Chemical Society, Brown, Lewis and Weber have outlined the procedures for calculating with sufficient accuracy the heat data needed for the correct design of equipment and for cracking operation. The deviation of the higher hydrocarbons from the perfect gas laws can be plotted against reduced pressures for a series of reduced temperatures. A paper by Lewis and Luke (1933) supplied a chart for making the isothermal correction to internal energy necessitated by deviation from the gas laws, and the enthalpy or

total heat can be corrected with the aid of curves given by Watson and Nelson (1933). Cracking involves mixtures of vapours and liquids, and the enthalpy of the mixtures may be calculated as the sum of the enthalpies of the components. By determining the true boiling-point curve of a stock, the molecular weight and the enthalpy of any weight fraction of the mixture per pound can be calculated. Fugacities of vapour and liquid at temperature and total pressure of equilibrium, shown in a plot of fugacity pressure *vs.* reduced pressure derived from the plot first mentioned above, may be used to calculate equilibrium of vapour and liquid, as a practical illustration shows.

Four variable factors enter into the results of the cracking operation for a given oil, the temperature, pressure, time and conversion per pass, the last depending on the combination of the other three. From a laboratory study in which each variable could be controlled, Sydnor reported [15] that with increasing conversion per pass the yield of gasoline decreased. Higher yields of gasoline were obtained at 200 lb. pressure than at 750 lb., whether the temperature was held at 860° or 900° F. Gasoline production fell off as temperature was increased, whilst pressure and conversion per pass were constant. Temperature was thought to be the controlling factor determining octane number under the conditions. With increasing conversion per pass the per cent. of light ends in the gasoline increased; or with conversion per pass constant, the per cent. of light ends increased as the temperature was raised.

From a somewhat similar study, however, based on cracking virgin Mid-Continent gas oil in a pilot plant by once-through operation, Keith, Ward, and Rubin [16] came to the conclusion that temperature apparently had no effect on octane number, but the greater the "crack per pass" the higher the octane number by either research or motor method. For a given gas-to-gasoline ratio the higher the pressure, the better the anti-knock value by the motor method. If cracking conditions are such as to hold tar production to a minimum, the general equation for a monomolecular reaction may be used to correlate the data if the amount of material cracked is expressed in terms of gasoline plus gas as a function of time. Over the range studied, pressure has no effect on rate of reaction. The amount of fixed gas produced per unit of gasoline varies inversely as the pressure. Nemtzov, who separated the cracking reaction into the specific elements combined in it,[17] says that the simple primary reaction of splitting molecules is unaffected by pressure, since it is monomolecular. The chances for condensation between molecules split off increase as the square of the pressure. In high-pressure liquid-phase cracking, "diene" concentration is low and the gasoline is relatively stable. The thermopolymerisation of olefins, diolefins and acetylene is homogeneous and bimolecular, and is accelerated by pressure increase. If the composition of the hydrocarbon mixture and the other conditions are assumed to be constant, pressure aids in the formation of aromatic hydrocarbons. Dehydrogenation of aliphatic hydrocarbons would be inhibited by pressure. On the basis of present general ideas on the mechanism of pyrogenic reactions, it may be assumed that pressure must increase the formation of *iso*-compounds. Reforming or cracking *under pressure* will produce more *iso*-compounds in the gasoline, it may be predicted on theoretical grounds, than reforming under other identical conditions but at atmospheric pressures.

Sakhanov and Tilicheev, giving a general view of the subject of cracking,[18] say with reference to pressure that it does not affect the yield of gasoline nor the velocity of cracking unless it be at a late stage of the cracking. Its importance lies in affording better heat transfer, and excessive pressures are unnecessary for that purpose. Higher pressures " must " be used for cracking light stocks such as kerosines than for " mazout," for example.

Data furnished by Butkov and Chechkina [19] upon the heat input required for cracking are as follows, starting with Baku kerosine distillate at 20° C. : to crack at 625° C., 941–944 cal. per kg. ; at 675°, 1052–1095 cal. ; and at 725°, 1284–1337 cal. Molecular weights of a number of cracked distillates from Mid-Continent gas oils for use in designing equipment were determined by FitzSimons and Thiele.[20] Benzene was the preferred solvent in the cryoscopic work. An alignment chart was designed by Zimmerman for calculating weight balances in skimming and cracking operations.[21] Computations were made of the composition of the liquid obtained by the fractional condensation of gas produced in cracking kerosine under vacuum. This was done by Murray's method, and the results agreed well with the actual material balance.[22]

VI. Liquid–Vapour-Phase Cracking.

A. Non-Catalytic.

In a review of the development of commercial cracking processes by Rosendahl,[23] the Holmes–Manley process is said to be characterised by long operating time, and points are enumerated which relate to measures intended to prevent heavy deposits of coke from forming. Deposits of highly polymerised material on the walls of the chamber are to be removed before they coke, residuum from the reaction chamber is to be passed through a colloid mill before re-cycling, coke separation is to be controlled by electric current, spiral notchings in the heated tubes are to keep the oil in turbulent motion, the apparatus is to be lined with special metals, etc. From their observations on the operation of a Winkler–Koch cracking unit, Korovatzkii and Frolova [24] reported a gain in the yield of 200° E.P. gasoline of 1·5 per cent. or of 3·7 per cent. for 225° E.P. by raising the temperature of the transfer at the outlet of the high-pressure coil from 491° to 494° C. A single measurement of temperature at this point cannot, however, be relied on for accuracy. Korovatzkii and Sokolova also experimented with a Jenkins cracking unit at Grozny, and gave 33 per cent. of gasoline as the best obtainable yield. In some comparisons between the operations of a Grozny and a Knowles coking oven made by Tarasov, Aleksandrov and Popova [25] it appeared that the Knowles oven coke contained more ash and less volatile and moisture than the other. More gasoline was obtained in making coke by the Knowles process. Heavy fractions of Tarakan crude oils were cracked at pressures from 50 to 300 atmospheres.[26] Above 400° C. and 200 atmospheres, coke and gas losses were high. The cracking reaction slowed down as the pressure was raised, the yield of gasoline diminished, and the gasoline was less unsaturated.

Flexibility in cracking is illustrated in a Dubbs cracking unit at Quaker State refinery at Farmer's Valley, Pa.[27] In a 26-day run it cracked, in turn, gas oil, naphtha, gas oil and petrolatum without being taken off gasoline

production as the changes in charging stock were made. The Pennzoil Co. used its Dubbs reforming unit for cracking gasoline to convert kerosine distillate into high anti-knock gasoline.[28] A highly paraffinic gas oil is being cracked in a Dubbs plant of the most modern full-flashing design at the Allen, Okla., refinery of the Sunray Oil Co. Fifty-three per cent. of 396° F. end-point gasoline is produced, with an octane number of 69. The unit has also operated on Allen crude oil.[29] A 500-brl. Dubbs cracking plant forming part of the new equipment of the Big West Oil Co., Montana, produces in addition to motor fuel a cracked residue of an A.P.I. gravity of 5-6° and viscosity of 150 seconds Furol, its b.s. is less than 0·2 per cent. by the benzole centrifuge method. Gas oil and fuel oil have been charged as well as the heavy oil for which the plant was designed.[30] Low-temperature coal tar and the tar acids from it, as well as shale oil and lignite tar, readily yield motor fuel by cracking, as Fisher and Morrell found.[31] High-temperature coal tar and the tar acids from it are very refractory cracking stocks. Ryabov claims that benzole can be produced in yields similar to those of gasoline from petroleum oils by cracking cleaned coal oils at carefully selected narrow ranges of temperature, pressure, and time.[32] Besides the usual high-pressure apparatus, a Dubbs unit operating in Rumania is equipped with a superheater for the residuum and two expansion chambers in which alternately coke is deposited.[33] A pressure of about 30 lb. per sq. in. is maintained in the coking chambers. The superheater supplies to the residuum the heat expended in vaporising the oil, and is the means by which the quality of the coke is controlled. The coke is in no way inferior to that produced in non-residuum operation at high pressure. In 31 days' continuous operation the coking chamber was filled thirty-two times. A paraffinic residuum yielded 22 per cent. of coke. The new refinery of the Creditul-Minier in Ploesti also has a low-pressure coking unit included in its modern Dubbs plant.[34]

B. Catalytic.

Low-temperature brown-coal tars high in paraffins yielded 45 per cent. gasoline when they were cracked with the aid of floridin, or, for the medium and lower-boiling tar fractions, activated coke.[35] The tar vapours at 375–475° C. were passed over the catalyst at atmospheric pressures with from 20 to 100 per cent. of steam. Pressure did not increase the yield, but lowered the optimum temperature of reaction by 50°. Potassium silicate on active carbon or pumice is a cracking catalyst.[36] A solution of potassium carbonate containing small amounts of potassium silicate, chloride and sulphate is used also for impregnating the same or similar carriers.

VII. Vapour-Phase Cracking.

A. Non-Catalytic

The "True Vapour Phase" cracking plant is described by Holland and Sachs[37] as follows: The charging stock is vaporised by heating and flashing, superheated to dryness and subjected to a temperature just below the cracking temperature in a second section of the tube-still heater and then mixed with heat-carrier gas for cracking. This gas is heated to 1,100° F., just above the cracking temperature, in one of three blast-furnace stoves by

contact with hot checker brick. By this treatment little cracking takes place before the intended temperature is reached, it is claimed, because of the speed with which the superheating is accomplished, and the method of cracking by the heat in the carrier gas is calculated to secure equalisation of temperature. Gas and coke production is said to be minimal.

Attention is again called by Wagner, in a discussion of vapour-phase cracking, to the primary importance of time and temperature as factors in this type of operation. The physical and chemical properties of the charging stock are entirely secondary.

Petrove and his associates [38] applied vapour-phase cracking to low-temperature tars from a Russian coal in the laboratory, and obtained a 26 per cent. yield of the light fraction when the temperature did not exceed 600–650° C. Low-temperature tar from Barzas sapropelites was equally good material for cracking in the vapour phase, and the light fractions were almost free of phenols. Hydrogenating the cracked residuum four times yielded 63 per cent. of gasoline. In their laboratory studies of high-temperature cracking, Butkov and Ostrovai [39] sought for the conditions that would be most productive of aromatic hydrocarbons. Vapour-phase cracking was limited to the process as conducted at temperatures of 570–620° C. Pyrolysis signified cracking at 670–700° C. Pyrolysis was preferred to vapour-phase cracking for producing aromatic hydrocarbons, high octane number, and a gasoline that could be refined without high losses. Some earlier work [40] had indicated from both laboratory and commercial-scale data that 700° C. was the optimum for producing aromatic hydrocarbons by cracking Surakhany paraffin mazout at atmospheric pressure. The yield of light oil remained nearly constant at 18 per cent. over a wide range of temperature, but the specific gravity rose with the temperature, and was close to 0·850 when cracking was conducted at 700°.

B. Catalytic.

Catalytic cracking (with 10 per cent. of $AlCl_3$) and catalytic dehydrogenation of the cracked gasoline fraction were applied by Zelinsky and Mikhlin [41] to Emba crude oil, Grozny paraffin and a sample of ceresin. It was possible to produce gasoline containing only open-chain compounds by removing both the aromatic hydrocarbons formed in the catalytic cracking and those produced by dehydrogenating the naphthenes. If only 5 or 8 per cent. of aluminium chloride was used, as much as 11 per cent. of unsaturated hydrocarbons was found in the cracked distillate from ceresin. The experimenters concluded that ceresin is formed from *cyclo*paraffins.

VIII. Combination Liquid–Vapour and Vapour-Phase Cracking.

What is known as the "Soviet" cracking unit, designed and constructed in the Union, is also "operated by men trained without the help of foreign technologists." [42] This unit has a capacity of 70–90 tons of gas oil per day, and is reported to have produced an aviation gasoline of 88–90 octane number. When reforming was applied to a mixture of Vickers pressure distillate, straight-run naphtha, and cracked distillate from the unit itself, the result was quite similar to the cracked distillate obtained in the vapour-

phase cracking at 600–605°. Operation could be continued without shut-down for 10 days. According to Andreyev,[43] the Soviet unit, which was originally designed for liquid-phase cracking, was able to produce an aviation gasoline of "110 octane number" by reforming a gasoline cracked in vapour phase, at 600° C. and "reduced pressure." The aviation gasoline contained 73 per cent. of aromatic and 20 per cent. of unsaturated hydrocarbons. By ordinary operating on gas oil, the gasoline contained 32 per cent. of aromatic hydrocarbons, 40 of olefins and 12 of naphthenes; and such a run continued for 48 days.

IX. Combination of Operation.

One of the increased developments of the cracking art in 1934 is the operation of cracking stills with multiple-coil cracking so that two or more operations may be carried out in one unit. Distillation of the crude oil, viscosity breaking, naphtha reforming and vapour-phase cracking can be provided for in the unit. Such achievements are credited by Armistead [44] to the development in laboratories of pilot or miniature plants in which study can be given to the fundamental factors in the heat treatment of petroleum oils and data for use in plant design could be collected. A unit described by Jirasek and Schaeffer [45] has the capacity for operating on 19,000 brl. of crude oil per day. The gasolines from the two separate cracking operations are stabilised and refined together. In the furnace of a unit operated by the Marathon Oil Co. at Fort Worth, a convection-tube bank is made to serve for both the viscosity-breaking coils and those in which so-called vapour-phase cracking takes place, but separate radiant heat sections are used.[46] A Dubbs unit of the Shell Oil Co. in Montreal has two cracking furnaces. The convection tubes in the larger furnace are graduated in surface area so that the rate of heating is uniform throughout the coil.[47] The largest reforming unit in the world, belonging to the Shell Petroleum Corp., East Chicago, Ind., operates a Dubbs unit the heater of which has a convection section for preheating the charge and a cracking-soaking section. Both cracking and soaking are by radiant heat.[48] The furnace of a Dubbs unit in the refinery of the Quaker State Oil Refining Corp. is divided into heating and soaking sections, separately fired. The oil passes first through a bank of convection tubes mounted between two bridge walls, is subjected to the action of radiant heat in the heating and soaking sections in turn, enters the reaction chamber at the top, emerges at the base and is flashed into the flash chamber. The Sinclair Company's Fort Worth refinery includes a cracking unit which was designed to operate on topped crude oil or gas oil or to reform naphtha converting it to gasoline of high octane number. This has a heater of the de Florez type. The gasoline in the wet gas from the top of the fractionating tower is absorbed in a gas-oil cut from the main tower. The gas is re-circulated through the tower, and the light gasoline is separated along with the pressure distillate.[49]

Tests of oil-still tubes showed improved physical properties and creep resistance when the carbon content was increased in a 4–6 per cent. chromium steel containing molybdenum. Slow cooling gave better creep resistance than normalising, the structure being more uniform. "Longitudinal" material proved to be more resistant to both creep and impact than

"transverse."[50] Barlow's formula may be applied to the calculation of the allowable inside diameter of cracking tubes. The minimum safe thickness of the tube walls is given by the formula $2T = \frac{O.D. \times P}{C.S.}$, where T is the minimum safe thickness in inches, O.D. is the outside diameter, P is the pressure in lb. per sq. in., and C.S. is the creep stress in lb. per sq. in.[51] There are advantages in using double pipe coils of special steels, from the standpoint of both economy and the properties of the metals. An inside tube of Sicromal D16 bonded to an outer one of Sicromal 8 is recommended.[52] A modernised Dubbs unit in the Pennzoil Co. refinery in Oil City, Pa., is equipped with a transfer-line heat exchanger constructed of Griscom-Russell Tubeflo sections. There are twelve of the sections, arranged in three parallel stacks each four high. The oil from the cracking furnace is reduced in temperature from 950° to 850° F.; and in its rapid flow through the Tubeflo sections the temperature is brought down to 700° F.[53] The four pumps used in the cracking operation at the Pennzoil refinery are all driven by gas engines, and their operation is so satisfactory that no standby pumps are considered necessary.

Forged reaction chambers are usually made by the Bethlehem Steel Co. from solid ingots of plain carbon steel. A large percentage of the original ingot is discarded before piercing it, in order to eliminate the faulty portions of the metal. Throughout the working, heat treatment and annealing, a complete record of temperatures and other data is kept. A smooth interior and high factors of safety are ensured. The Bethlehem Company claims that none of its hollow forgings has ever failed in service.[54] Return bends cast from an alloy have better creep properties than tubes rolled from the same alloy, possibly because the rolling tends to break up the interlocking of crystals. A small percentage of titanium added to a chrome–molybdenum alloy seems to give a less penetrable scale than the alloy without titanium, and so affords protection against corrosion.[55] An informing paper by White, Clark and Wilson[56] considers the qualifications and the testing of low-alloy steels for high-temperature service in petroleum refinery equipment. High resistance to oxidation and corrosion and stable structure are equally as essential as high creep strength, tensile and impact resistance. Instability of structure is usually manifested by the precipitation of carbides between the crystals.

X. By-Products.

The paper by Ellis[57] on the beginning of a petroleum chemical industry presents the subject as of that date. No other by-product of cracking is so ready a building material for synthesis as ethylene, propylene and butylenes, both from their availability in large volumes from the cracking process and from their chemical character. They are converted to alcohols, and the alcohols to esters and ketones. The olefins treated with chlorine give the dichlorides, or, if hypochlorous acid is used, chlorohydrins are the result; and either may be hydrolysed to the glycols. Ethylene glycol and the ethers and esters formed have found a great variety of uses. Ethylene in cracked gas can be concentrated by passing the gas through activated carbon.[58] At 700° C. ethylene has been converted into aromatic hydro-

carbons almost completely according to Dubois.[59] By thermal polymerisation, Storch and Atkinson [60] converted ethylene to a liquid boiling in the gasoline range. This was condensed by the aid of $AlCl_3$ to a more viscous oil, of which the best specimens had a viscosity index in the neighbourhood of 100. The oiliness, essential in lubricating oil, was assumed to be satisfactory from Nash, Stanley and Bowen's results. Only tentative conclusions are, however, claimed.

The particular amyl alcohol isomers produced from a gasoline cracked in vapour phase (at 680° C.) according to Pipik and Mezhebovskaya [61] depends in part on the concentration of H_2SO_4 used in hydrating the amylene. Secondary amyl alcohol mainly was formed when 75, and especially 80 or 85, per cent. acid was used. When divinyl, from kerosine, was rectified, about one-third of the fraction distilling between 28° and 50° C. proved to be dienes, with *cyclo*pentadiene predominating.[62] It is reported that 200,000 tyres were produced in Russia during 1933 by the polymerisation of butadiene from cracked gases.[63]

Acetylene produced by cracking hydrocarbon gases at temperatures above 800° C. can be hydrated to acetaldehyde by passing it through dilute sulphuric acid containing mercuric oxide as a catalyst; the acetaldehyde is readily oxidised to acetic acid. According to Ellis, one refinery in the United States is converting hydrocarbon gases to acetylene in the electric arc and making acetic acid from the acetylene.

Cracked gases usually contain the paraffins and olefins of one to five carbon atoms. The conversion of these hydrocarbons to " building stones " for synthesis, namely CH_3^-, CH_2^-, and CH^-, necessitates choosing medium conditions of operating, since the higher homologues need less heat to crack than the lower, and the time of reaction must not be long enough for the splitting off of hydrogen to go too far. Fifty-five per cent. of the theoretical yield of unsaturated hydrocarbons could be produced in an electrically heated porcelain tube with 50 per cent. of hydrogen added, sub-atmospheric pressure, a temperature of 1,100° C., and 0·02 second in the reaction chamber. If the temperature was raised and the reaction time was shortened, the yield could only be raised by preventing turbulent flow of the gas through the tube. If the flow was turbulent, part of the gas decomposed catalytically to carbon and hydrogen on the walls of the tube, whilst other parts were unchanged. The cracking could be better accomplished by passing the charge through a series of furnaces, each one operating at a higher temperature than the preceding.[64] A gas obtained by cracking petroleum in the vapour phase had a heating value of 11,000 cal. per g., and was too high in higher olefins to be used as city gas. By recracking in a retort filled with a refractory, the heating value was reduced more than 50 per cent., and more than 95 per cent. of the gas formed was made up of hydrogen, paraffins and nitrogen.[65] The Davis reforming process converts butane and other gases similarly high in calorific value to lower B.Th.U. gas. With the aid of nickel-wire catalyst in helical form packed in a refractory-lined chamber, it is said that the rich gas is cracked without tar and condensable oils being formed.[66] A neutral gas—that is, one that is neither carburising nor oxidising—can be made for use in heat-treating steels in muffle furnaces by heating " town or coke oven gas " to 900–1000° C. The higher the carbon content of the steel the higher must be the ratio of the methane to the

hydrogen in the neutral atmosphere, and this is readily controlled. The tubes are loosely packed with iron turnings, and as they become clogged with carbon the turnings are pushed out and replaced with fresh ones. This method has been found satisfactory in a continuous "strip normalizing furnace." The surface of the strip was not carburised. In a plant of the Woodall-Duckham Co., certain of the vertical carbonising retorts have been fitted with "trunks" placed in the top, the purpose of which is to force the coal to move into the carbonising zone at a faster rate. The gas evolved is cracked as it passes through the region of superheat between the retort wall and the trunk. There is no excessive deposit of carbon in the upper part of the retort, and hence no over-cracking. The tar is much more viscous than that produced without the "trunks." [67]

Oberle, in a paper about petroleum coke, recommends that an elastic "carpet" like mercury be laid in the reaction chamber between the residuum and the metal walls. Petroleum coke is described as an "alloy" of carbon and hydrocarbons.[68]

XI. 1934 Cracking Reviews.

In "The Development of the Cracking Art," Keith and Montgomery [69] trace the history of the art from the beginning, 1860, to 1924, with special attention to the physical and thermodynamic principles involved, the reason why certain charging stocks must be selected, and the difficulties overcome. At that point they say: "These conditions focused attention upon the design of a plant which would:

1. Handle distillate and residuum stocks with equal facility.
2. Decrease fixed charges by greater capacity.
3. Lower fuel consumption by more effective use of heat exchangers and hot oil pumps.
4. Utilise the excess heat for other purposes.
5. Fractionate the distillate into an end-point product.
6. Increase the length of run and improve the quality of the tar by preventing coke deposition.
7. Increase the yield by recovering all the gasoline fractions in the gas and reducing the tar to a minimum.
8. Offer greater ease and safety in operation."

The remainder of the paper describes the advances made in these directions since 1924 in the Gyro, de Florez, Dubbs and Cross operations. The Diamond Jubilee number of the *Oil & Gas Journal*, celebrating the discovery of petroleum in Pennsylvania, contains a short history of cracking [70] and a note by Dr. Burton [71] recalling some of his experiences in getting the Burton cracking process into operation 21 years before.[71] The Dubbs, True Vapour Phase and Gyro processes have been reviewed by Critchley,[72] but the bulk of the paper is occupied with a general consideration of reactions, energetics, thermodynamics and fundamental variables in cracking. Boehtlingk compiled a bibliography of Soviet patents on petroleum,[73] and Pimenov is said to have reviewed cracking and cracked products.[74]

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PROGRESS IN HYDROGENATION OF PETROLEUM AND ECONOMIC COMPARISON WITH CRACKING.

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Introduction.

Since results were last published in this *Journal* three years ago,[1] the major advances in petroleum hydrogenation have taken place in the production of gasoline from gas oils. This article will therefore be concerned exclusively with this phase of the process.

In previous papers [1, 2] operation of the hydrogenation process was described whereby gasolines of high octane number were obtained by conducting the reaction at high temperatures and under such conditions that the extent of the hydrogenation was limited so as to form stable but non-paraffinic products. Since this time, new catalysts have been developed which, owing to their greater activity, promote the conversion of gas oils to gasoline at temperatures lower than those employed in the operation described above. Moreover, these catalysts permit greater throughputs, afford higher yields, with the result that their use is more favourable economically. The information herein presented is grouped into two major divisions: experimental results in "low" temperature hydrogenation with highly active catalysts, and an economic comparison of hydrogenation with cracking.

Experimental Hydrogenation Results with Highly Active Catalysts.

The results reported in this section were obtained in experimental hydrogenation units of about two barrels per day capacity. It should be pointed out, however, that catalysts of the type used in this work have been employed in large-scale operation for some time by the I.G. Farbenindustrie, and will be used in the vapour-phase units of the coal hydrogenation plant of the Imperial Chemical Industries in Great Britain.

The significance of the greater activity of the new catalysts as compared with those formerly used is that high conversion to gasoline may be obtained at low temperatures. Thus gasoline yields considerably above 100 per cent. by volume are realized without sacrifice in capacity. Although the gasoline so made is of poorer octane number than the product of high-temperature hydrogenation, it has exceptional lead susceptibility (on the average 1·5 lead susceptibility factor on the scale of Hebl *et al.*),[3] and is a stable and refined product except for the necessity of a caustic wash to remove dissolved hydrogen sulphide.

Operation for low-temperature gasoline hydrogenation is apparently optimum when approximately 70 per cent. conversion per pass is obtained to 400° F. [204·5° C.] end-point gasoline. The remaining material (about

* Standard Oil Development Co. † Standard Oil of Louisiana.

40 per cent. on total feed) is a water-white, hydrogenated gas oil, lower-boiling than the original feed, which, because of its paraffinic character, high colour, and negligible sulphur content, is suitable for Diesel fuels and high-grade gas oils, or as a cracking stock of excellent quality. Alternatively, the hydrogenated gas oil may be re-cycled to the hydro unit.

The re-cycle operation was studied quite completely on a wide variety of feed stocks. The results obtained are comparable with what would be realized in large-scale units. Once-through operation, while not studied on as many feed stocks as in re-cycle operation, has also been investigated.

Re-cycle Operating Results.—The salient characteristics of some of the feed stocks studied are tabulated below.

Feed Stock.	A.P.I. Gravity.	Specific Gravity.	Avg. B.* Pt.	Aniline Pt.	Remarks.
Light Cycle Gas Oil	21·5	0·9250	464° F. (240° C.)	52° F. (11° C.)	Very refractory cracked stock.
California Cycle Gas Oil	22·4	0·9195	546° F. (285·5° C.)	77° F. (25° C.)	Refractory cracked stock.
Heavy Coastal Feed	24·7	0·9060	640° F.† (338° C.)	157° F. (69·5° C.)	Approximately 70 per cent. of Coastal Crude, over 14·5 per cent. bottoms.
Venezuela Gas Oil	25·1	0·9035	549° F. (287° C.)	106° F. (41° C.)	Mixed virgin-and-cracked stock.
East Texas Gas Oil	26·4	0·8960	800° F.‡ (426·5° C.)	203° F. (95° C.)	Approximately 15 per cent. cut on E. Texas Crude, over 15 per cent. bottoms.
Naphtha Bottoms	32·4	0·8635	475° F. (246° C.)	113° F. (45° C.)	Cracked stock.
East Texas Gas Oil	35·7	0·8465	546° F. (285·5° C.)	163° F. (73° C.)	Approximately 11 per cent. cut on E. Texas Crude, above paraffin dist.

* Volumetric average boiling point, approximately equal to 50 per cent. point.
† 50 per cent. point.
‡ 50 per cent. point estimated from distillation at 10 mm. pressure.

It will be noted that the feed stocks selected show an extreme variation in characteristics—from highly aromatic (50° F. [10° C.] aniline point) to very paraffinic (203° F. [95° C.] aniline point)—from comparatively low boiling (471° F. [244° C.] avg. boiling point) to very high boiling (50 per cent. at 800° F. [426·5° C.]),—from a comparatively narrow virgin cut (35·7 E. Texas gas oil, 11 per cent. on crude) to a wide cut of the crude (70 per cent., of Coastal Crude).

Hydrogenation results on these stocks are shown in Table I. All the runs in this table were made at a throughput of 2·2 volumes of fresh feed plus cycle stock per volume of catalyst per hour. Temperature in the reactor was controlled so as to maintain 60 per cent. fresh feed (by volume) in the total feed to the unit. In addition, special gasoline work-ups are presented in Table II, showing treating and stabilization results for the runs tabulated in Table I.

Based on the results shown in these tables, it is estimated that finished,

	Cycle Gas Oil.		Calif. Cycle.		Heavy Coastal.		Venez. Gas Oil.		E. Texas Heavy Gas Oil.		Naphtha Bottoms.		E. Texas Gas Oil.	
Feed Stock :														
Total feed, vol./vol./hr.		2·2		2·2		2·2		2·2		2·2		2·2		2·2
Per cent. fresh feed		65·5		61·0		60·9		58·5		60·6		60·4		62·2
Per cent. vol. yield dist. on fresh feed		122·5		119·4		118·2		116·0		117·0		113·8		114·2
Raw Distillate Inspection :														
A.P.I. gravity		59·9		59·1		63·2		66·1		65·1		63·1		65·5
Specific gravity		0·7395		0·7426		0·7270		0·7160		0·7195		0·7270		0·7185
Initial, ° F.		95 (35° C.)		101 (38·5° C.)		102 (39° C.)		97 (36° C.)		100 (38° C.)		100 (38° C.)		95 (35° C.)
D. & L. at 122° F. (50° C.)		6·5		6·0		3·0		8·5		4·0		5·5		7·0
Per cent. at 140° F. (60° C.)		7·5		5·5		7·5		11·0		6·5		8·0		9·0
,, 158° F. (70° C.)		13·5		10·0		14·0		17·5		12·0		14·0		15·0
,, 212° F. (100° C.)		31·5		28·0		34·0		39·0		31·5		32·5		33·0
,, 284° F. (140° C.)		56·5		55·0		62·5		72·0		61·0		61·5		60·0
,, 356° F. (180° C.)		78·5		78·0		86·5		93·0		86·0		86·0		84·0
,, 374° F. (190° C.)		85·5		84·0		91·5		—		92·0		92·0		89·0
90 per cent. at ° F.		386 (196·5° C.)		396 (202° C.)		368 (186·5° C.)		339 (170·5° C.)		370 (188° C.)		367 (186° C.)		378 (192° C.)
Final b. pt., ° F.		417 (214° C.)		428 (220° C.)		404 (206·5° C.		374 (190° C.)		407 (208·5° C.)		397 (203° C.)		413 (211° C.)
Recovery, per cent.		96·0		95·0		98·0		94·8		97·0		96·5		95·5
Residue, per cent.		1·0		1·0		1·0		1·4		1·0		1·1		1·0
Colour, Saybolt		+30		+28S		+30S		+30		+30		+30S		+30
Aniline point, ° F.		140 (60° C.)		141 (60° C.)		146 (60·5° C.)		146 (63·5° C.)		152 (66·5° C.)		143 (61·5° C.)		150 (65·5° C.)
Octane No. at 212 *		60·6		55·5		57·0		61·1		48·7		55·4		51·6
Feed or Cycle Stock Inspection :	Feed.		Feed.		Feed.		Feed.		Feed.		Feed.		Feed.	
A.P.I. gravity	21·5	38·3	23·4	40·1	24·7	41·7	25·1	45·3	26·4	45·1	32·4	45·2	35·7	46·0
Specific gravity	0·9250	0·8335	0·9195	0·8245	0·9060	0·8170	0·9035	0·8005	0·8960	0·8010	0·8635	0·8010	0·8468	0·7970
Initial, ° F.	388 (198° C.)	397 (203° C.)	196 (91° C.)	418 (214·5° C.)	428 (220° C.)	428 (220° C.)	360 (183° C.)	378 (192° C.)	378 (192° C.)	430 (221° C.)	404 (206·5° C.)	409 (209·5° C.)	386 (196·5° C.)	429 (219·5° C.)
5 per cent. at ° F.	430	412	357	439	474	448	448	396	686	452	428	425	478	452
10 ,, ,,	440	418	410	444	493	452	470	400	698	458	432	429	494	458
20 ,, ,,	448	419	460	451	522	459	491	404	—	465	440	434	510	464
30 ,, ,,	454	424	490	456	554	463	506	410	—	475	446	437	522	472
40 ,, ,,	460	428	504	463	590	471	516	415	—	485	459	442	534	479
50 ,, ,,	464 (240° C.)	432 (222° C.)	526 (274·5° C.)	470 (243·5° C.)	640 (338° C.)	480 (249° C.)	536 (280° C.)	420 (215·5° C.)	—	497 (258·5° C.)	468 (242° C.)	448 (231° C.)	547 (286° C.)	488 (253·5° C.)
60 ,, ,,	470	437	546	480	684	490	554	425	—	513	480	454	556	500
70 ,, ,,	478	444	568	492	—	505	580	435	—	536	493	463	568	514
80 ,, ,,	486	454	600	511	—	533	610	448	—	573	510	476	580	529
90 ,, ,,	502	470	643	542	—	583	652	470	—	638	523	499	598	551
95 ,, ,,	519	486	678	571	—	627	676	494	—	—	555	520	616	567
Final b. pt., ° F.	556 (291° C.)	512 (266·5° C.)	97 % at 700 (371° C.)	603 (317° C.)	—	647 (341·5° C.)	684 (362° C.)	536 (280° C.)	18% at 700 (371° C.)	688 (364·5° C.)	605 (318·5° C.)	555 (290·5° C.)	640 (338° C.)	583 (306° C.)
Recovery, per cent.	99·0	98·5	97·0	98·5	—	97·2	98·5	97·4	—	96·1	99·0	98·5	98·5	98·2
Colour, Saybolt or Robinson	16½R	+27	16R	+26S	8½R	+30S	11R	+30	16R	+29	10½R	+30S	18½R	+29S
Aniline point, ° F.	52 (11° C.)	160 (71° C.)	77 (25° C.)	171 (77° C.)	157 (69·5° C.)	174 (79° C.)	106 (41° C.)	170 (76·5° C.)	203 (95° C.)	195 (90·5° C.)	113 (45° C.)	175 (79·5° C.)	163 (73° C.)	190 (88° C.)
Sulphur, per cent.	—	—	0·680	—	0·200	—	0·864	—	—	—	0·278	—	0·122	—

* Series 30 Engine at 212° F. Jacket, 600 r.p.m. and 200 lb./sq. in. compression.

stabilized gasolines of the following yields would be obtained in large-scale re-cycle operation from the feed stocks shown :

	Cycle Gas Oil.	Calif. Cycle.	Heavy Coastal.	Venez. Gas Oil.	E. Texas Heavy Gas Oil.	Naphtha Bottoms.	E. Texas Gas Oil.
Feed Stock :							
° A.P.I. gravity	21·5	22·4	24·7	25·1	26·4	32·4	35·7
Specific gravity	0·9250	0·9195	0·9060	0·9035	0·8965	0·8635	0·8465
Average b. pt., ° F.	471	546	640	549	800	475	546
,, ° C.	244	285·5	338	287	426·5	246	285·5
Aniline point, ° F.	50	77	157	106	203	113	163
,, ,, ° C.	10	25	69·5	41	95	45	73
Throughput, vol./vol./hr.	2·2						
Per cent. fresh feed	60						
Per cent. vol. yield of finished stabilized gasoline	119	117	117	115	115	113	112
Gasoline Inspection (Stabilized and Finished) :							
° A.P.I. gravity	58·0	59·0	62·0	60·0	64·0	63·0	65·0
Specific gravity	0·7465	0·7430	0·7315	0·7390	0·7240	0·7280	0·7200
D. & L. at 122° F. (50° C.)	6	6	4	6	4	6	7
,, 140° F. (60° C.)	9	9	8	9	8	11	12
Per cent. at 212° F. (100° C.)	29	30	33	32	31	32	34
,, 284° F. (140° C.)	56	57	62	60	60	60	63
90 per cent. point, ° F. (° C.)	370° F. (188° C.)						
Final b. pt., ° F. (° C.)	400° F. (204·5° C.)						
Reid v. p., lb./sq. in.	8·5	8·5	8·0	8·5	8·0	9·0	9·5
Octane No. C.F.R.*	61	58	57	57	48	54	52
,, ,, + 1 ml. Pb.	74	71	70	69	61	68	68
Colour	+30	+30	+30	+30	+30	+30	+30
Preformed gum	None.						
Copper dish gum	Less than 3 mg./100 ml.						
Sulphur, per cent.	Less than 0·03.						

* C.F.R. Motor Method (A.S.T.M. standard procedure).

It will be noted that in all cases more than 110 per cent. of finished gasoline is obtained from the feed. It may be said of all these gasolines, produced from an extreme range of feed stocks, that :

(*a*) They require no treating except a caustic wash to insure passing the corrosion and doctor tests.

(*b*) They are high in colour (+ 30), have virtually no gum, and are low in sulphur (less than 0·03 per cent.).

(*c*) They have normal distillation characteristics in spite of the very aromatic quality of some of the feed stocks.

(*d*) Although the gasolines are of medium octane numbers, they are highly susceptible to tetraethyl lead, resembling in this respect the most lead-susceptible straight-run gasolines (see also Table VI).

The foregoing discussions have been concerned largely with the production of 400° F. [204·5° C.] end-point hydrogasoline. Other types of operation also have interesting possibilities. A run was made on one of the feed stocks (Naphtha Bottoms) for 300° F. [149° C.] end-point gasoline. The results were 50 per cent. fresh feed and 114 per cent. yield of distillate. When this gasoline was stabilized so that it had less than 10 per cent. distilled at 146° F. [63·5° C.] and was under 7 lb. Reid vapour pressure, the loss incurred reduced the yield to approximately 100 per cent. (vs. 114 per cent. unstabilized gasoline yield from the unit). The properties of the stabilized gasoline are briefly summarized in Table III.

Particularly noteworthy are : (*a*) the good octane number (62·9 C.F.R.), (*b*) the high lead susceptibility (76·2 O.N. with 1 ml. lead), (*c*) the low acid heat (1·5° F. [0·83° C.]), and (*d*) the absence of any copper dish gum.

This grade of aviation gasoline may also be expected from other feed stocks—with somewhat better octane numbers on the more aromatic feeds, and somewhat poorer octane numbers on the more paraffinic.

TABLE II.

Special Work-ups showing Treating and Stabilization Results for Hydrogenation Runs shown in Table I.

	Cycle Gas Oil.	Calif. Cycle.	Heavy Coastal.	Venez. Gas Oil.	E. Texas Heavy Gas Oil.	Naphtha Bottoms.	E. Texas Gas Oil.
Feed Stock :							
Aniline point, ° F.	52 (11° C.)	77 (25° C.)	157 (69·5° C.)	106 (41° C.)	203 (95° C.)	113 (45° C.)	163 (73° C.)
Average b. pt., ° F.	464 (240° C.)	546 (285·5° C.)	640° (338° C.)	547 (286° C.)	18% at 700 (371° C.)	475 (246° C.)	546 (285·5° C.)
° A.P.I. gravity	21·5	22·4	24·7	25·1	26·4	32·4	35·7
Specific gravity	0·9250	0·9195	0·9060	0·9035	0·8960	0·8635	0·8465
Special Distillate Work-up (washed with Na_2CO_3 and/or Doctor Solution) :							
° A.P.I. gravity	57·7	58·5	62·2	63·8	63·7	63·0	66·3
Specific gravity	0·7480	0·7445	0·7305	0·7245	0·7250	0·7275	0·7155
D. & L. at 122° F. (50° C.)	5·0	3·5	5·0	4·7	2·5	6·5	8·0
" 140° F. (60° C.)	8·5	5·5	9·5	12·0	4·5	11·5	13·0
Per cent. at 212° F. (100° C.)	28·0	27·5	33·5	35·0	28·0	32·5	35·0
Per cent. at 284° F. (140° C.)	55·5	57·0	61·5	71·0	58·0	59·5	64·0
90 per cent. point at ° F.	370 (188° C.)	390 (199° C.)	378 (192° C.)	340 (171° C.)	374 (190° C.)	372 (189° C.)	372 (189° C.)
Final b. pt., ° F.	400 (204·5° C.)	428 (220° C.)	406 (208° C.)	380 (193·5° C.)	414 (212° C.)	396 (202° C.)	407 (208·5° C.)
Dist. loss, per cent.	3·0	1·0	2·0	3·0	1·0	3·0	3·0
Colour, Saybolt	+30	+30	+30	+30	+30	+30	+30
Pref. gum, mg./100 ml.	0·0	0·2	0·0	0·1	—	0·0	0·0
Copper dish gum, mg./100 ml.	1·2	3·6	2·4	0·4	—	1·1	0·6
Breakdown time, mins.	240+	240+	240+	240+	240+	240+	240+
Doctor	Pass	Pass	Pass	—	Pass	Pass	Pass
Corrosion	Pass	—	Pass	Pass	Pass	—	Pass
Sulphur, per cent.	0·010	0·018	0·016	0·014	—	0·020	0·018
Aniline point, ° F.	136 (58° C.)	141 (60·5° C.)	140 (60° C.)	144 (62° C.)	151 (66° C.)	143 (61·5° C.)	153 (67° C.)
Octane No. C.F.R. (M.M.)	61·4	54·8	58·2	59·4	44·3	55·5	53·0
Octane No. C.F.R. (M.M.) + 1 ml. lead	75·0	67·0	71·5	71·8	56·5	70·0	69·8
Stabilization Work-up :							
Distillate caught under ice (snap sample) :							
Per cent. C_3 (vol.)	1·21	1·67	—	1·59	0·95	—	—
" C_4 (vol.)	9·32	6·00	—	9·31	5·65	—	—
" C_5 (vol.)	9·71	7·83	—	10·25	7·92	—	—
" C_6 (vol.)	79·76	84·50	—	78·85	85·48	—	—
Reid v. p., lb./sq. in.	13·4	11·4	—	13·6	9·8	—	—
Light ends removed :							
Per cent. C_3 (vol.)	1·2	1·7	—	1·6	1·0	—	—
" C_4 (vol.)	2·0	0·0	—	2·0	0·0	—	—
Reid v. p., lb./sq. in.	10·1 †	7·8	—	10·2 ‡	7·8	—	—

° 50 per cent. point, ° F. † Apparently too high; estimated at 8·5 lb.
‡ Apparently too high; estimated at 9·0 lb.

Once-Through Operating Results.—Although fewer feed stocks have been run in once-through operation, the results so obtained are in good agreement with what would be expected from re-cycle operation. Complete data for several once-through experimental runs with the same type of catalysts as used in the re-cycle work are shown in Table IV.

It will be observed from these results that the gasoline produced by once-through operation, as with re-cycle hydrogenation, show high colour,

low sulphur and normal distillation characteristics. They likewise require no treatment except a caustic wash and have high lead susceptibilities.

Once-Through Operation for By-Products such as Kerosine, Range Oil and Diesel Fuel.—Owing to the efficient hydrogenation of the catalysts employed, gas oils of high aniline point are produced in once-through operation, even from aromatic stocks. For example, in Table IV, Naphtha Bottoms

TABLE III.

Production of Aviation Gasoline by Re-cycle Hydrogenation using Highly Active Catalysts.

	Naphtha Bottoms.
Feed Stock :	
° A.P.I. gravity	32·4
Specific gravity	0·8635
Average b. pt., ° F.	468 (242° C.)
Aniline point, ° F.	113 (45° C.)
Conditions and Results :	
Total feed, vol./vol./hr.	2·2
Per cent. fresh feed	50
,, yield of finished, stabilized * aviation gasoline	100
Octane No. C.F.R. (M.M.)	62·9
,, ,, + 1 c.c. lead (M.M.)	76·2
,, ,, + 2 c.c. lead (M.M.)	80·4
Per cent. at 124° F. (51° C.)	1·5
,, 146° F. (63·5° C.)	9·0
,, 158° F. (70° C.)	18·0
,, 284° F. (140° C.)	98·0
Colour	+30
Copper dish gum, mg./100 ml.	0
Acid heat, ° F.	1·5
Reid v. p., lb./sq. in.	6·9

* Less than 10 per cent. at 140° F. (60° C.), and less than 7 lb. Reid v. p.

of 114° F. [45·5° C.] An. Pt. yielded a gas oil of 174° F. [79° C.] An. Pt. and 43·5° A.P.I. [0·8086]. As an additional example, operation on heavy Venezuelan fractions showed the results presented in Table V when operated primarily for Diesel oil. The high gravities (A.P.I.) along with the high aniline points indicate that these gas oils are of the paraffinic or paraffinic-naphthenic type, with virtually no unsaturation. The sulphur contents are apparently as low as those of the corresponding gasolines (less than 0·03 per cent.). It should be particularly noted that these gas oils meet all requirements for a high-quality Diesel fuel with such properties as (*a*) high paraffinicity, (*b*) water-white colour, (*c*) low pour, and (*d*) low sulphur.

All of the above properties indicate excellent possibilities for the production of high grades of kerosine, of range oil, etc. The simplest method of operation would be a once-through process, in which the overhead could be worked up, for instance, into 375° [190·5° C.] end-point gasoline, a kerosine cut, and/or a Diesel fuel.

ECONOMIC COMPARISON OF HYDROGENATION WITH CRACKING.

General Bases.—The following general bases have been used in studying the economic value of hydrogenation for gasoline production :

(1) The oil refinery considered is either a new one, or one that has need of additional facilities for gasoline production.

(2) The gasoline is to be produced by running a given crude to ultimate

TABLE IV.

Once-through Hydrogenation Results for Production of Gasoline from Gas Oils using Highly Active Catalysts.

	Naphtha Bottoms.		E. Texas Gas Oil.		Virgin Venez. Gas Oil.	
Total feed, vol./vol./hr.	2·2		2·2		2·2	
Per cent. vol. yield of gaso. on feed	73·4		71·7		56·0	
Per cent. vol. yield of gas oil on feed	38·4		35·8		53·6	
Per cent. vol. yield of total product on feed	111·8		107·5		109·6	
Raw Gasoline Inspection :						
°A.P.I. gravity	59·8		63·3		67·2	
Specific gravity	0·7395		0·7265		0·7120	
Initial, ° F.	89 (31·5° C.)		88 (31° C.)		93 (34° C.)	
D. & L. at 122° F. (50° C.)	7·5		7·1		8·9	
,, 140° F. (60° C.)	10·0		10·6		14·6	
Per cent. at 158° F. (70° C.)	11·5		11·0		17·0	
,, 212° F. (100° C.)	26·0		27·5		43·0	
,, 284° F. (140° C.)	50·5		55·5		87·5	
,, 356° F. (180° C.)	78·0		82·5		—	
,, 374° F. (190° C.)	84·5		88·5		—	
90 per cent. at ° F.	382 (194·5° C.)		381 (194° C.)		293 (145° C.)	
Final b. pt., ° F.	401 (205° C.)		404 (206·5° C.)		327 (164° C.)	
Recovery, per cent.	95·5		95·5		94·3	
Residue, per cent.	0·8		0·9		0·9	
Octane No. C.F.R. (M.M.)	54·8		—		66·6	
Aniline point, ° F.	142 (61° C.)		149 (65° C.)		141 (60·5° C.)	
Sulphur, per cent.	0·019		—		—	
Colour, Saybolt	+308		+308		+308	
Gas Oil Bottoms or Feed Inspections :	Feed.		Feed.		Feed.	
°A.P.I. gravity	32·1	43·5	36·7	45·2	29·0	43·1
Specific gravity	0·8650	0·8085	0·8415	0·8010	0·8815	0·8105
Initial, ° F.	395 (201·5° C.)	415 (213° C.)	370 (188° C.)	436 (224·5° C.)	442 (228° C.)	335 (168·5° C.)
5 per cent. at ° F.	420	431	439	460	473	368
10 ,, ,,	432	434	456	465	479	378
20 ,, ,,	440	438	480	471	496	392
30 ,, ,,	449	443	499	479	513	406
40 ,, ,,	459	448	512	486	532	420
50 ,, ,,	470 (243·5° C.)	453 (234° C.)	525 (274° C.)	494 (256·5° C.)	550 (288° C.)	436 (224·5° C.)
60 ,, ,,	482	460	537	504	569	454
70 ,, ,,	496	468	550	516	587	475
80 ,, ,,	513	481	566	531	604	502
90 ,, ,,	540	502	588	550	625	547
95 ,, ,,	563	523	607	568	639	583
Final b. pt., ° F.	598 (314·5° C.)	548 (286·5° C.)	640 (338° C.)	584 (306·5° C.)	652 (344·5° C.)	613 (323° C.)
Recovery, per cent.	98·5	98·5	98·0	98·0	98·0	97·7
Aniline point, ° F.	114 (45·5° C.)	174 (79° C.)	158 (70° C.)	190 (88° C.)	136 (58° C.)	168 (75·5° C.)
Colour, Saybolt or Robinson	11½R	+278	+108	+268	17½R	+258
Sulphur, per cent.	0·281	—	0·105	—	0·90	—

yield. Two typical crudes are considered herein : East Texas and West Texas. The ultimate gasoline yield is obtained in either of two ways :

Case A.—By an ordinary refinery procedure; namely distillation, gas oil cracking and reduced crude cracking. This is referred to as "*Cracking only.*"

Case B.—By a variation of the above method, in which a cycle gas oil is withdrawn from the gas oil cracking coils and processed

by once-through hydrogenation (at "low" temperature, using highly active catalysts), the hydro gas oil produced being returned to the cracking coils. This is referred to as "*cracking plus hydrogenation.*"

(3) The composite gasolines produced in Case A and Case B are equal in quantity, are both brought up to 70 octane number C.F.R. (M.M.) by tetra-ethyl lead, have a Reid vapour pressure of 10 lb., approximately the same volatility, and 400° F. [204·5° C.] end-point. The fuel oil produced is of the same gravity in the two cases, and of nearly the same viscosity (less than 150 Furol at 122° F. in all cases), although the fuel oil in Case A (cracking only) is somewhat less viscous.

TABLE V.

Once-through Hydrogenation Results for Production of Gasoline and Paraffinic Diesel Fuel from Venezuelan Heavy Gas Oil.

Feed Stock :		
° A.P.I. gravity	19·3	18·5
Specific gravity	0·9385	0·9435
10 mm. dist.—		
Initial b. pt., ° F.	416 (213·5° C.)	432 (222° C.)
50 per cent. at	502 (261° C.)	521 (271·5° C.)
95 ,,	579 (304° C.)	590 (310° C.)
Per cent. sulphur	1·74	1·7
Products :		
Gasoline (raw, unstabilized)—		
Per cent. yield on feed	36·5	20·5
Initial b. pt., ° F.	95 (35° C.)	106 (41° C.)
D. & L. at 140° F. (60° C.)	6·8	5·5
Per cent. at 158° F. (70° C.)	7·2	7·0
,, 212° F. (100° C.)	23·0	30·5
Final b. pt., ° F.	380 (193·5° C.)	340 (171° C.)
Octane No. C.F.R. (M.M.)	59	60
Colour, Saybolt	+30	+30
Gas Oil—		
Per cent. yield on feed	75·2	87·8
° A.P.I. gravity	36·2 0·8440	35·0 0·8500
Aniline point, ° F.	183 (84° C.)	188 (86·5° C.)
Initial b. pt., ° F.	404 (206·5° C.)	374 (190° C.)
10 per cent. at ° F.	451 (233° C.)	433 (223° C.)
50 ,, ,,	567 (297° C.)	606 (319° C.)
Per cent. at 700° F. (371° C.)	88·7	77
Colour, Saybolt	+17	+22
Per cent. sulphur	0·03	0·02
Pour, ° F.	−40	−40

(4) This comparison is based on a new hydrogenation plant embodying the latest simplifications in design gained through experience with the commercial hydro plants of the Standard Oil Company (N.J.) and the I.G. Farbenindustrie A.-G. These improvements and simplifications include :

(*a*) Elimination of large excess capacity in the hydrogen producing units, based on tests on commercial equipment.

(*b*) Use of one large hydrogenation unit of 6045 barrels * per day feed rate employing one large reaction drum rather than two units of several reactors each.

(*c*) Reduction in the number of units of moving equipment by use of units of large capacity.

(*d*) Reduction in the amount of piping, in view of (*a*), (*b*) and (*c*). Less expensive alloy tubing is used for high-pressure lines in view of its satisfactory resistance to hydrogen and sulphur attack in the commercial units of the I.G. Farbenindustrie A.-G. Building requirements are likewise less, in addition to the reduction effected by consolidation of all pumps, compressors, gas boosters, etc., in one structure.

(*e*) Advantage has been taken of increased capacity available in the equipment used for scrubbing carbon dioxide from the raw hydrogen. This increase is based on improvements demonstrated by operation of commercial equipment.

It is assumed in this study that hydrogen will be manufactured from low sulphur natural gas. Where natural gas is not available, a small increase in investment is necessary for operation on refinery or hydro-plant release gas. The plant costs used are based on American construction and material costs. It should be pointed out that the hydro unit assumed in this estimate may be used for lubricating oil or kerosine production by adjustment of operating conditions and character of feed stock.

(5) Cracking operations are based on the use of large-size modern equipment. For example, gas oil cracking is assumed as being carried out on high pressure units of approximately 30,000 brl./day total feed rate. Other refinery operations, such as crude distillation, are likewise premised on modern large-size equipment. Plant costs are based on American conditions.

(6) In order to fix definite quantities, the starting point taken is the capacity of the hydro plant; namely, 6045 barrels of feed per calendar day. The quantity of crude required to produce this feed stock is next calculated; and then the ultimate yield of products from this amount of crude is estimated. Thus the material flow-plan for Case B (cracking plus hydrogenation) is completed (see Figs. 2 and 5). Next the situation is considered where this same total gasoline production is made by Case A (cracking only). This involves more crude running, more distillation, more fuel oil production, etc. (see Figs. 1 and 4).

(7) Since equal quantities of gasoline of the same quality are produced in the two cases, the economic picture is arrived at from a consideration of crude and fuel reduction, and the increase in overall operating and overall investment † costs in Case B over Case A. The estimates for operating and investment costs, although made as consistent as possible for the two set-ups, are undoubtedly subject to variations depending on local conditions as well as on general business trends. The operating costs for Case A

* In this paper one barrel represents 42 U.S. gallons or 35 Imperial gallons.

† This includes operating and investment costs for hydrogenation (in Case B), cracking, distillation, absorption, stabilization, treating, steam and power generation, water pumping, etc.

TABLE VI.

Volatility and Octane-number Balance for East Texas and West Texas Crudes.

Naphtha from:	Yield on Crude.	Per cent. at 158° (70° C.).	Per cent. at 212° (100° C.).	Reid Vapour Pressure, lb.	Octane No. C.F.R. (M.M.).	Lead Suscept. ibility Factor.*
EAST TEXAS.						
Case A—Cracking Only:						
Straight run, 400° F. (204·5° C.) E.P.	35·0	15	34	8·5	57·5	1·3
Gas oil cracking	28·9	25	39	14	65	0·80
Reduced crude cracking	2·1	19	31·5	11	61·2	0·70
Butane loss	−1·3	−115	−100	−60	−112	−1·6
Total gasoline	64·7	17·5	35·0	10·0	59·9	1·05
Case B—Cracking plus Hydrogenation:						
Straight run, 400° F. (204·5° C.) E.P.	35·0	15	34	8·5	57·5	1·3
Gas oil cracking	21·3	25	39	14	65	0·80
Reduced crude cracking	2·1	19	31·5	11	61·2	0·70
Hydrogenation	10·5	12	30	8·5	57	1·5
Cracking hydro gas oil	4·6	22	36	12·5	70	1·0
Butane loss	−0·6	−115	−100	−60	−112	−1·6
Total gasoline	72·9	17·0	34·5	10·0	60·0	1·14
WEST TEXAS.						
Case A—Cracking Only:						
Straight run, 400° F. (204·5° C.) E.P.	28·4	6	24	6	56·5	0·8
Gas oil cracking	26·1	25	39	14	70	0·6
Reduced crude cracking	4·1	19	31·5	11	67	0·5
Butane loss	− 0·1	−115	−100	−60	−112	−1·6
Total gasoline	58·5	15·0	31·0	9·8	63·2	0·69
Case B—Cracking plus Hydrogenation:						
Straight run, 400° F. (204·5° C.) E.P.	28·4	6	24	6	56·5	0·8
Gas oil cracking	19·7	25	39	14	70	0·6
Reduced crude cracking	4·3	19	31·5	11	67	0·5
Hydrogenation	10·2	11	29	8·5	59·5	1·5
Cracking hydro gas oil	4·2	22	36	12·5	71	1·0
Butane loss	−0·1	−115	−100	−60	−112	−1·6
Total gasoline	66·7	14·0	30·5	9·4	62·6	0·84

* According to Hebl, Rendel and Garton.

(cracking only) and Case B (cracking plus hydrogenation) were calculated as follows:

(*a*) Direct operating costs, less fuel and utilities, were estimated for each unit operation. *Overhead* and indirect costs were not included*, since they differ markedly from refinery to refinery.

* A 10 per cent. direct overhead on labour has, however, been included.

(*b*) The estimated requirements of fuel, steam, electric power and water were summed up for the two cases; and the costs of these utilities was expressed as a function of fuel cost. The *capital investments required for the utilities were estimated and added to the total other investments.* In arriving at the utility investments, it has been assumed that the utility plants would be either an addition to or a fraction of a large utility plant located in a large refinery.

(8) The final comparison sums up the following differences for the two cases:

(*a*) Operating cost: Hydrogenation costs more.
(*b*) Fuel credit: Hydrogenation has less credit.
(*c*) Crude purchased: Hydrogenation saves crude.
(*d*) Total investment: Hydrogenation has higher investment.

Thus, for any given crude and fuel price, hydrogenation will show a definite saving or loss in dollars per day. This, in turn, is expressed as a per cent. return on the added investment in the case of hydrogenation. (It may be noted here that the estimated direct costs include no depreciation in any case.)

East Texas Crude.—Figs. 1 and 2 show diagrammatically the flow-plan for handling East Texas Crude by "cracking only" and by "cracking plus hydrogenation." Table VI presents the volatility and octane-number balance for each of the cases.

It will be noted that the cracked gasoline in either case is not acid-treated or clay-finished, but only stabilized and treated with a small quantity of inhibitor. If any treating of the cracked distillate were considered necessary, this circumstance would favour the hydrogenation set-up, since a smaller proportion of cracked gasoline is produced therein.

No investment is allowed for oil tankage, refinery oil lines or pump house. Such equipment is estimated to be approximately the same in both cases. Similarly, investment and operating costs for sweetening have been omitted from the two set-ups, since identical quantities of gasoline are produced.

The hydro plant on the basis of the data presented effects a saving in crude of 5087 B/D and a reduction in merchantable fuel oil of 3562 B/D. The advantage (or disadvantage) for hydrogenation is shown graphically in Fig. 3 as the per cent. return on the added investment for hydrogenation, from which the following tabulation is abstracted:

*Per cent. Return on Added Investment * in the Case of Hydrogenation.*

Fuel Oil Realization.	40 c./Brl.	70 c./Brl.	$1.00/Brl.
Delivered Price of East Texas Crude:			
(*a*) $1.00/brl. . . .	46 per cent.	19 per cent.	−9 per cent.
(*b*) $1.20/brl. . . .	63 „	36 „	8 „
(*c*) $1.40/brl. . . .	80 „	52 „	25 „

* Including all attendant facilities.

The advantage for hydrogenation obviously increases with increasing spread between crude price and fuel oil realization.

It should be noted that not only the fuel oil produced, but also the gas

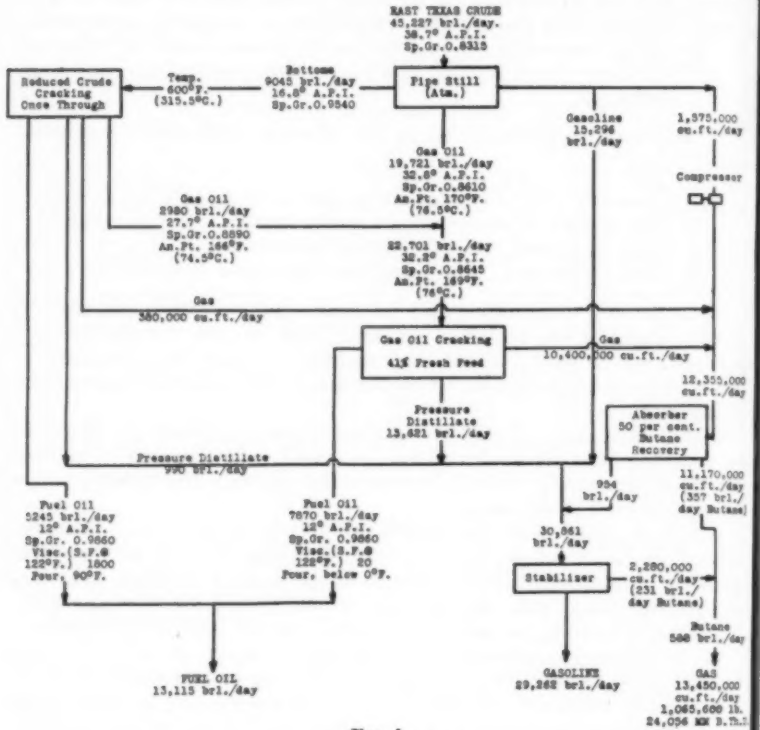
EAST TEXAS CRUDE
45,227 brl./day.
38.7° A.P.I.
Sp.Gr.0.8315
Reduced Crude Cracking Once Through
Temp. 600°F. (315.5°C.)
Bottoms 9045 brl./day 16.8° A.P.I. Sp.Gr.0.9540
Pipe Still (Atm.)
Gasoline 15,296 brl./day
1,375,000 cu.ft./day
Compressor
Gas Oil 19,721 brl./day 32.6° A.P.I. Sp.Gr.0.8610 An.Pt. 170°F. (76.5°C.)
Gas Oil 2980 brl./day 27.7° A.P.I. Sp.Gr.0.8890 An.Pt. 166°F. (74.5°C.)
22,701 brl./day 32.2° A.P.I. Sp.Gr.0.8645 An.Pt. 169°F. (76°C.)
Gas 380,000 cu.ft./day
Gas Oil Cracking 41% Fresh Feed
Gas 10,400,000 cu.ft./day
12,355,000 cu.ft./day
Pressure Distillate 13,621 brl./day
Absorber 50 per cent. Butane Recovery
Pressure Distillate 990 brl./day
934 brl./day
11,170,000 cu.ft./day (357 brl./day Butane)
Fuel Oil 3245 brl./day 12° A.P.I. Sp.Gr. 0.9860 Visc.(S.F.@ 122°F.) 1800 Pour, 90°F.
Fuel Oil 7870 brl./day 12° A.P.I. Sp.Gr. 0.9860 Visc.(S.F.@ 122°F.) 20 Pour, below 0°F.
30,861 brl./day
Stabiliser
2,280,000 cu.ft./day (231 brl./day Butane)
Butane 588 brl./day
FUEL OIL 13,115 brl./day
GASOLINE 29,262 brl./day
GAS 13,450,000 cu.ft./day 1,065,600 lb. 24,056 MM B.Th.U.

FIG. 1.

FLOWSHEET FOR CRACKING ONLY OF EAST TEXAS CRUDE.

Final Yields and Inspections.

Gasoline.		*Fuel Oil.*	
Yield, per cent. (vol.)	64·7	Yield, per cent. (vol.)	29·0
Gravity :		Gravity :	
° A.P.I.	60·0	° A.P.I.	12·0
Sp. gr.	0·7390	Sp. gr.	0·9860
Reid vapour pressure, lb.	10·0	Visc. (S.F.) at 122° F.	70
Per cent. at 158° F. (70° C.)	17·5	Pour	30° F.
" 212° F. (100° C.)	35·0		
Final b. pt.	400° F. (204·5° C.)	*Gas.*	
		Yield, per cent. (wt.)	8·10
Octane No. C.F.R. (M.M.)	59·9	B.Th.U./cu. ft.	1785
ml. T.E.L./gal./70 O.N.	1·2		
Inhibitor, lb./1000 gal.	0·118		

was credited at fuel oil realization price. This was a distinct advantage to the " cracking only " case, since an excess of gas was produced in that set-up above the fuel requirements. However, in a large balanced refinery

this gas would likely be consumed. If, on the other hand, this gas could not be utilized, hydrogenation would be benefited, when fuel is worth 70 c./brl., to an increase in the return on the added hydro investment, at $1.00 crude, from 19 to 31 per cent.

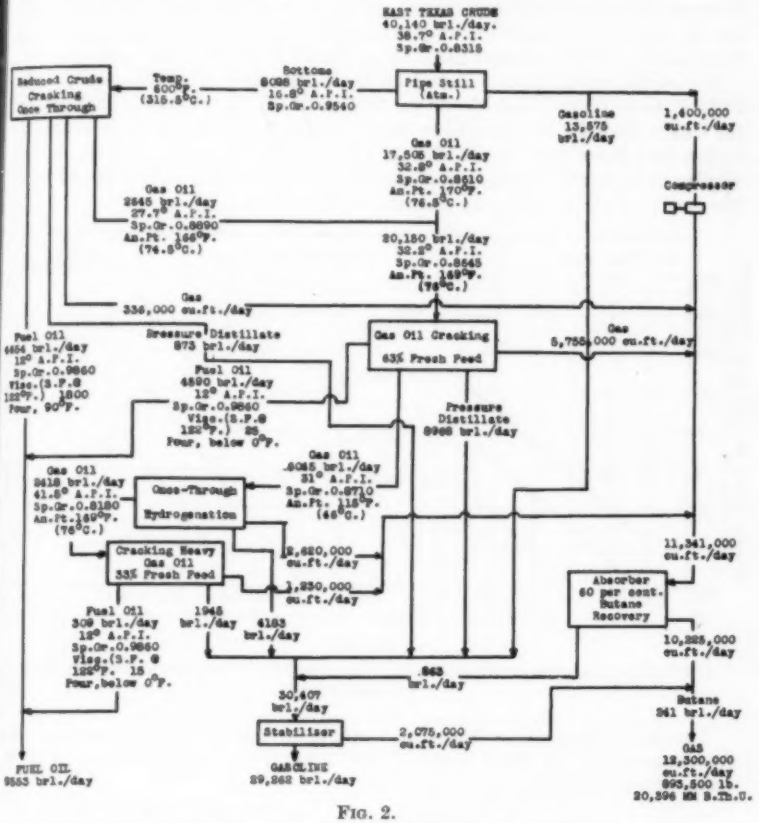
EAST TEXAS CRUDE
40,140 brl./day.
38.7° A.P.I.
Sp.Gr.0.8318
Reduced Crude Cracking Once Through
Temp. 600°F. (315.5°C.)
Bottoms 8026 brl./day 16.8° A.P.I. Sp.Gr.0.9540
Pipe Still (Atm.)
Gasoline 13,875 brl./day
1,400,000 cu.ft./day
Gas Oil 17,505 brl./day 32.8° A.P.I. Sp.Gr.0.8610 An.Pt. 170°F. (76.5°C.)
Compressor
Gas Oil 2845 brl./day 27.7° A.P.I. Sp.Gr.0.8690 An.Pt. 166°F. (74.5°C.)
20,180 brl./day 32.2° A.P.I. Sp.Gr.0.8645 An.Pt. 169°F. (76°C.)
Gas 336,000 cu.ft./day
Fuel Oil 6454 brl./day 12° A.P.I. Sp.Gr.0.9860 Visc.(S.F.@ 122°F.) 1800 Pour, 90°F.
Pressure Distillate 873 brl./day
Gas Oil Cracking 63% Fresh Feed
Gas 5,758,000 cu.ft./day
Fuel Oil 4590 brl./day 12° A.P.I. Sp.Gr.0.9860 Visc.(S.F.@ 122°F.) 25 Pour, below 0°F.
Pressure Distillate 8906 brl./day
Gas Oil 2418 brl./day 41.8° A.P.I. Sp.Gr.0.8180 An.Pt.169°F. (76°C.)
Once-Through Hydrogenation
Gas Oil 8045 brl./day 31° A.P.I. Sp.Gr.0.8710 An.Pt. 115°F. (46°C.)
12,620,000 cu.ft./day
11,341,000 cu.ft./day
Cracking Heavy Gas Oil 33% Fresh Feed
1,230,000 cu.ft./day
Absorber 60 per cent. Butane Recovery
Fuel Oil 309 brl./day 12° A.P.I. Sp.Gr.0.9860 Visc.(S.F.@ 122°F. 15 Pour,below 0°F.
1945 brl./day
4183 brl./day
10,825,000 cu.ft./day
863 brl./day
30,407 brl./day
Butane 241 brl./day
Stabilizer
2,075,000 cu.ft./day
Gas 12,300,000 cu.ft./day 995,500 lb. 20,396 MM B.Th.U.
FUEL OIL 9553 brl./day
GASOLINE 29,262 brl./day

FIG. 2.

FLOWSHEET FOR CRACKING PLUS HYDROGENATION OF EAST TEXAS CRUDE.

Final Yields and Inspections.

Gasoline.		*Fuel Oil.*	
Yield, per cent. (vol.)	72·9	Yield, per cent. (vol.)	23·8
Gravity :		Gravity :	
° A.P.I.	60·0	° A.P.I.	12·0
Sp. gr.	0·7390	Sp. gr.	0·9860
Reid vapour pressure, lb.	10·0	Visc. (S.F.) at 122° F.	120
Per cent. at 158° F. (70° C.)	17·0	Pour	35° F.
,, 212° F. (100° C.)	34·5		
Final b. pt.	400° F. (204·5° C.)	*Gas.*	
		Yield, per cent. (wt.)	7·6
Octane No. C.F.R. (M.M.)	60·0	B.Th.U./cu. ft.	1660
ml. T.E.L./gal./70 O.N.	1·05		
Inhibitor, lb./1000 gal.	0·080		

West Texas Crude.—Flowsheets (Figs. 4 and 5) are presented for West Texas Crude, comparable to the case of East Texas Crude. Volatility and octane-number balances are shown in Table VI. A significant difference is that the gasoline, both straight-run and cracked, requires acid-treating because of the high sulphur content. In the "cracking plus hydrogenation" set-up, no acid-treatment is required either for the hydro gasoline or for that portion of the cracked gasoline produced from the hydro gas oil.

Somewhat more crude is saved by hydrogenation with this crude; viz. 5924 B/D of West Texas Crude *vs.* 5087 B/D of East Texas. The reason for this is that the less paraffinic West Texas Crude gives a more aromatic hydro feed stock (90° F. [32° C.] *vs.* 115° F. [46° C.] aniline point), which results in a greater yield advantage for hydrogenation as compared with the cracking yield on the same stock.

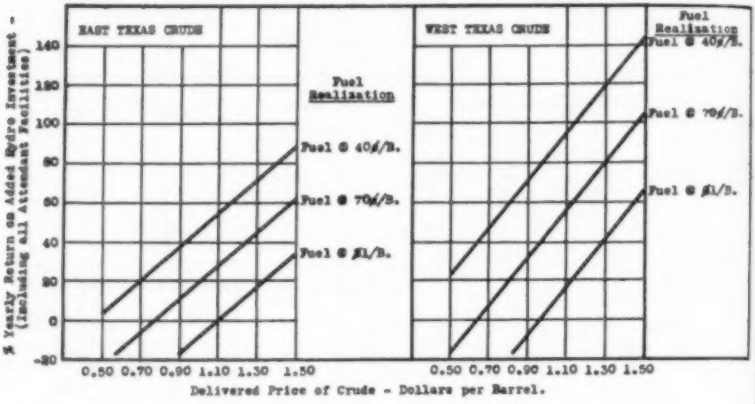

FIG. 3.

ESTIMATED ECONOMIC COMPARISON OF CRACKING ONLY VERSUS CRACKING PLUS HYDROGENATION.

The final comparison between "cracking only" and "cracking plus hydrogenation" of West Texas Crude is set forth graphically in Fig. 3, from which the following is taken:

Per cent. Return on Added Investment in the Case of Hydrogenation.*

Fuel Oil Realization.	40 c./Brl.	70 c./Brl.	$1.00/Brl.
Delivered Price of West Texas Crude:			
(*a*) $0.80/brl. . . .	59 per cent.	19 per cent.	−21 per cent.
(*b*) $1.00/brl. . . .	83 ,,	43 ,,	4 ,,
(*c*) $1.20/brl. . . .	108 ,,	68 ,,	28 ,,

* Including all attendant facilities.

As with East Texas Crude, the advantage for hydrogenation increases with increasing spread between crude and fuel oil. If West Texas and

East Texas Crudes were of the same price, the West Texas case would, of course, be more advantageous for hydrogenation. However, East Texas

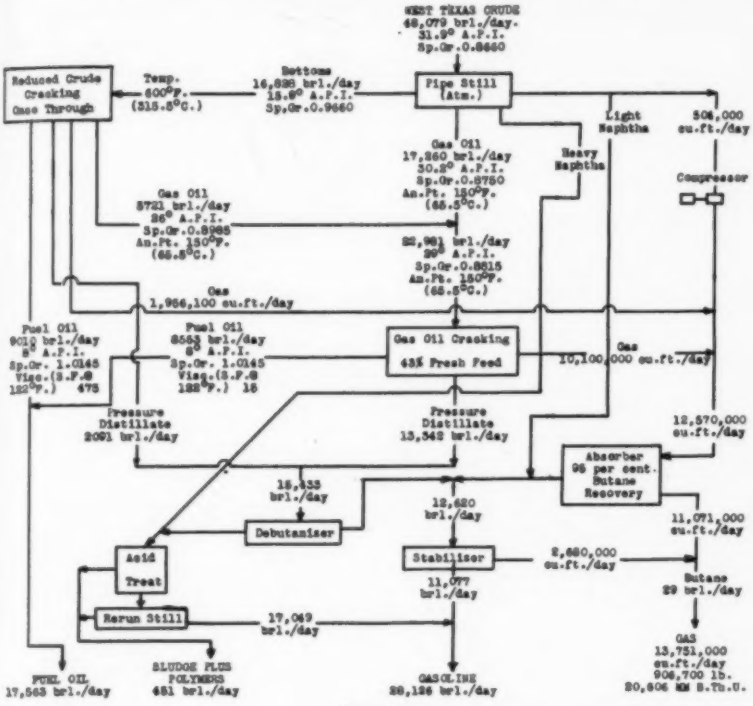

FIG. 4.

FLOWSHEET FOR CRACKING ONLY OF WEST TEXAS CRUDE.

Final Yields and Inspections.

Gasoline.		*Fuel Oil.*	
Yield, per cent. (vol.)	58·5	Yield, per cent. (vol.)	36·53
Gravity :		Gravity :	
° A.P.I.	59·0	° A.P.I.	8·0
Sp. gr.	0·7430	Sp. gr.	1·0145
Reid vapour pressure, lb.	9·8	Visc. (S.F.) at 122° F.	60
Per cent. at 158° F. (70° C.)	15·0	Pour	below 30° F.
" 212° F. (100° C.)	31·0		
Final b. pt.	400° F. (204·5° C.)	*Gas.*	
		Yield, per cent. (wt.)	6·23
Octane No. C.F.R. (M.M.)	63·2	B.Th.U./cu. ft.	1500
ml. T.E.L./gal./70 O.N.	1·25		
Sulphur, per cent.	0·095	*Sludge and Polymers.*	
		Yield, per cent. (vol.)	0·94

Crude is normally higher priced, and this differential must be considered in comparing the two cases. For example, with a fuel price of 70 c./brl. and East Texas Crude at $1.20/brl. delivered, the corresponding cost of

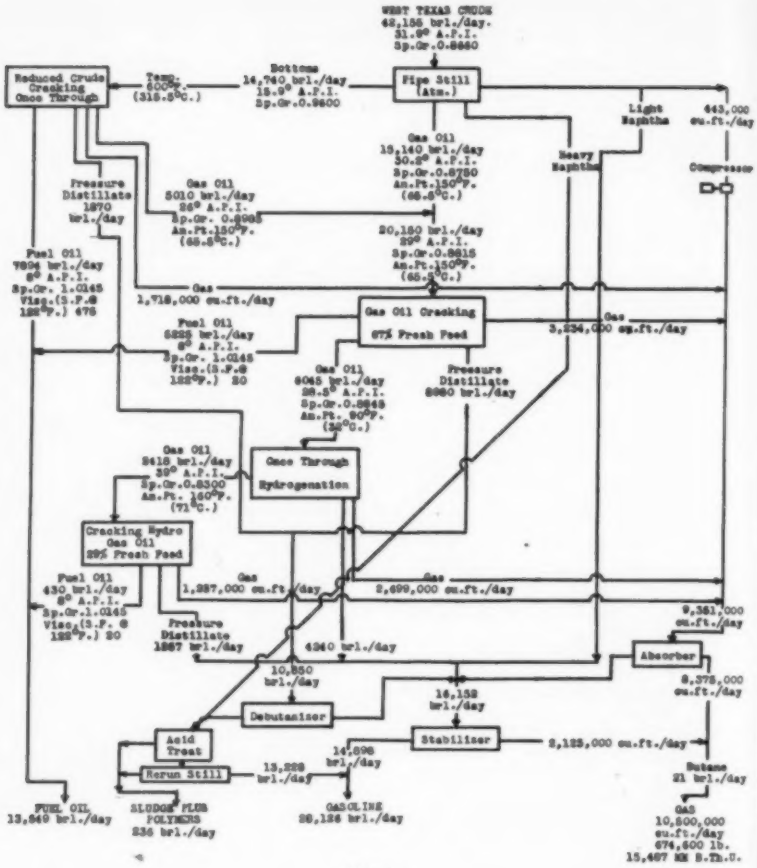
WEST TEXAS CRUDE
42,155 brl./day.
31.9° A.P.I.
Sp.Gr.0.8660
Pipe Still (Atm.)
Reduced Crude Cracking Once Through
Temp. 600°F. (315.5°C.)
Bottoms 14,740 brl./day 15.9° A.P.I. Sp.Gr.0.9600
Light Naptha
443,000 cu.ft./day
Heavy Naptha
Compressor
Gas Oil 19,140 brl./day 30.2° A.P.I. Sp.Gr.0.8750 An.Pt.150°F. (65.5°C.)
Pressure Distillate 1870 brl./day
Gas Oil 5010 brl./day 26° A.P.I. Sp.Gr. 0.8965 An.Pt.150°F. (65.5°C.)
20,150 brl./day 29° A.P.I. Sp.Gr.0.8815 An.Pt.150°F. (65.5°C.)
Fuel Oil 7924 brl./day 8° A.P.I. Sp.Gr. 1.0145 Visc.(S.F.@ 122°F.) 475
Gas 1,718,000 cu.ft./day
Gas Oil Cracking 67% Fresh Feed
Gas 3,234,000 cu.ft./day
Fuel Oil 8225 brl./day 8° A.P.I. Sp.Gr. 1.0145 Visc.(S.F.@ 122°F.) 20
Gas Oil 6045 brl./day 28.5° A.P.I. Sp.Gr.0.8845 An.Pt. 90°F. (32°C.)
Pressure Distillate 6980 brl./day
Gas Oil 8418 brl./day 29° A.P.I. Sp.Gr.0.8300 An.Pt. 160°F. (71°C.)
Once Through Hydrogenation
Cracking Hydro Gas Oil 29% Fresh Feed
Fuel Oil 430 brl./day 8° A.P.I. Sp.Gr.1.0145 Visc.(S.F. @ 122°F.) 20
Gas 1,287,000 cu.ft./day
Gas 2,699,000 cu.ft./day
9,351,000 cu.ft./day
Pressure Distillate 1867 brl./day
4340 brl./day
Absorber
10,850 brl./day
8,375,000 cu.ft./day
16,152 brl./day
Debutanizer
Stabilizer
3,123,000 cu.ft./day
Acid Treat
Rerun Still
14,896 brl./day
13,228 brl./day
Butane 21 brl./day
FUEL OIL 13,949 brl./day
SLUDGE PLUS POLYMERS 236 brl./day
GASOLINE 26,126 brl./day
GAS 10,500,000 cu.ft./day 674,600 lb. 15,467 MM B.Th.U.

FIG. 5.

FLOWSHEET FOR CRACKING PLUS HYDROGENATION OF WEST TEXAS CRUDE.

Final Yields and Inspections.

Gasoline.		*Fuel Oil.*	
Yield, per cent. (vol.)	66·72	Yield, per cent. (vol.)	32·14
Gravity :		Gravity :	
° A.P.I.	59·8	° A.P.I.	8·0
Sp. gr.	0·7430	Sp. gr.	1·0145
Reid vapour pressure, lb.	9·4	Visc. (S.F.) at 122° F.	90
Per cent. at 158° F. (70° C.)	14·0	Pour	below 30° F.
,, 212° F. (100° C.)	30·5		
Final b. pt.	400° F. (204·5° C.)	*Gas.*	
Octane No. C.F.R. (M.M.)	62·6	Yield, per cent. (wt.)	5·28
ml. T.E.L./gal./70 O.N.	1·08	B.Th.U./cu. ft.	1475
Sulphur, per cent.	0·095	*Sludge and Polymers.*	
		Yield, per cent. (wt.)	0·56

West Texas Crude is 94 c./brl. delivered to give the same interest return for hydrogenation (36 per cent. on added hydro investment).

Interpretation of Foregoing Economic Comparisons.

The results of the economic studies outlined above may be summarized as follows :

(1) Hydrogenation plus cracking becomes attractive over cracking alone (3-year payout on added investment) when a price differential of approximately 47 c./brl. exists between the delivered price of East Texas (or similar) Crude and the realization of fuel oil. For West Texas or similar high-sulphur crudes the differential between crude and fuel for which hydrogenation appears attractive is around 22 c./brl. Such differentials are now current in certain areas. Although the bases of estimate are necessarily of a general nature, and hence subject to local modification, the economic position of hydrogenation is shown to be due primarily to the price spread between crude and fuel.

(2) The attractiveness of hydrogenation is increased by charging the more aromatic (hydrogen-deficient) feed stocks.

(3) It is, of course, unlikely that the bases taken for economically comparing " cracking only " with " cracking plus hydrogenation " will apply in their entirety to any given refinery. However, it is believed that the final conclusions would not necessarily change appreciably even with considerable departures from the manufacturing methods shown or from the costs and investments taken. The reasons are :

(*a*) The advantage for hydrogenation fundamentally resides in the increased gasoline yield of hydrogenation over cracking. This means that the attractiveness for hydrogenation is enhanced by choosing the most aromatic clean feed stock feasible of production. The same high-pressure hydrogenation equipment is used whether the feed stock be aromatic or paraffinic. While the aromatic stock consumes more hydrogen, requiring more facilities for making and compressing the added hydrogen—yet this increment cost of hydrogen is small in comparison to the relatively higher gasoline yield (*vs.* cracking) on the more aromatic stock. In line with this reasoning, the hydro operation is preferably once-through (instead of re-cycle) because the hydro cycle stock is more paraffinic than the fresh feed. (The reverse is true in the case of high-temperature hydrogenation.)

(*b*) In order to emphasise how the economic comparison is more dependent on crude and fuel prices than on operating costs, the case may be cited for East Texas Crude. If the direct processing costs less fuel and utilities were increased by 100 per cent., the change could be wiped out by an increase in crude price of approximately 12 c./brl. with a fixed fuel price (since hydrogenation saves 5087 B/D of crude).

(*c*) The investment costs might appear to need considerable modification in most cases, since the basis used herein is that additional new equipment is needed at every point—which would apply exactly only to a new refinery. However, changes made in this

item will probably not represent a considerable percentage difference from the cases presented, since the additional investment over "cracking only" is due preponderantly to the large investment for the hydrogenation plant (including catalysts). Therefore, other investment costs may be varied somewhat without appreciably affecting the overall difference in capital costs for the two cases.

Several other features of the comparison between "cracking only" and "cracking plus hydrogenation" should be carefully noted:

(1) Although the flow-sheets indicate quantities of crude upward of 40,000 B/D, it is not necessary that such a quantity of any particular crude be actually run. But since the economic picture depends on the correct evaluation of the 6045 B/D of hydro feed, which is in each case (East Texas and West Texas) a cracked cycle stock, a scheme is presented whereby such a quantity of feed stock could be logically produced. If, for example, a more aromatic (or more refractory) feed stock can be produced in a given refinery (from whatever source) than was shown in the East Texas case (115° F. [46° C.] aniline point, 31° A.P.I. [S.G. 0·8708] gravity), and if East Texas is the marginal crude in the refinery, then hydrogenation should be more advantageous than calculated in this report.

(2) Both the East Texas and West Texas cases involve the use of tetraethyl lead to reach 70 octane number C.F.R. (M.M.) on the total gasoline. Owing to the high lead susceptibility (Table VI) of the hydro gasolines, a considerable credit is taken in the "cracking plus hydrogenation" set-up.

Alternative schemes would be to make octane number by either (*a*) naphtha reforming sufficient to bring the total gasoline up to 70 octane number, or (*b*) naphtha reforming to some optimum octane number using lead to bring the final octane number to 70. Since the total gasoline in the hydrogenation case contains a larger portion of straight-run plus hydro gasoline (characteristics similar in general to straight run) than in the "cracking only" case, it should be possible to effect the octane improvement in the hydro case by reforming a larger volume of naphtha to a smaller octane number improvement per gallon, which would result in lower costs and less degradation to gas.

It is believed, therefore, that although the economics of reaching 70 octane number will vary with the amount of reforming done and the price structure obtaining, there will be in practically all cases an advantage for hydrogenation.

Flexibility of Hydrogenation Process.

Perhaps one of the principal advantages of the hydrogenation unit, although not susceptible of concrete evaluation, is the extreme flexibility of the process, and its ability to make products of unusual quality. Thus in the case of once-through hydrogenation, not only is the gasoline sulphur free (0·03 per cent.) and highly stable, but also the hydro gas oil is sulphur free, water-white, highly paraffinic and suitable for premium Diesel fuel. Moreover, the hydrogenation unit, by change only in feed-stock and operating conditions, is capable of producing lubricating oils, kerosines, solvents,

etc., thus aiding the refiner in meeting variations in demand for the different refinery products.

The hydrogenation unit is likewise adaptable to keeping pace with the latest developments in cracking. Thus, if recent laboratory experiments in once-through cracking at very high temperatures are realized on a plant scale, the very refractory gas oils produced could well be processed once-through in the hydrogenation plant in either of two ways: (*a*) to approximately 70 per cent. gasoline and 40 per cent. gas oil yield (as outlined herein); or (*b*) primarily for maximum gas oil yield to produce a non-refractory feed stock for the high-temperature cracking unit. Method (*b*) would obviously involve less hydrogen, and hence less cost than method (*a*).

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NATURAL GAS AND NATURAL GASOLINE.

By THELMA HOFFMAN.

THE marketed production of natural gas, which had increased through 1930 but declined in 1931 and 1932, showed little change in 1933. The decrease in output from 1930 to 1933 was due, primarily, to the curtailment of industrial activity, with consumption by domestic and commercial users increasing steadily. In 1933 domestic and commercial consumption showed its first decrease, whilst the consumption for industrial purposes showed a gain.[1]

1933.	cu. ft.	
Production	1,555,474,000,000	
Consumption (production plus imports minus exports)	1,553,399,000,000	
field purposes	494,459,000,000	(32 per cent.)
domestic and commercial	368,774,000,000	(24 per cent.)
manufacture of carbon black	186,781,000,000	(12 per cent.)
public utility power plants	102,601,000,000	(7 per cent.)
fuel in petroleum refineries	66,333,000,000	(4 per cent.)
other industrial uses	334,451,000,000	(21 per cent.)

Whilst statistics for 1934 are not yet complete, it is believed that there has been an increase in production over 1933. Construction work on pipe-lines was at a standstill in 1933, with very little change in 1934.

Since a knowledge of the solubility of natural gases in crude petroleum is of importance in learning the mechanism of underground formations and in estimating oil reserves, A.P.I. has included this work in its research programme as Project 37.[2] The flow of gas against varying back pressures, as in the case of the flow from gas sand, has been investigated. Development of electrical apparatus which will indicate and predict pressure distribution after the initial or flush production has subsided will no doubt be of great assistance in estimating gas flow.[3]

In some of the gas fields in the eastern United States the rock pressure is very high. Various types of control are employed in order to obtain a pressure reduction from rock to line pressure. All these types of control are based on restricting velocities through regulators, restricting orifices, choke valves or small diameter tubes, with modifying devices [4] such as the alcohol bottle. This last, used with a restriction plate, makes it possible to reduce the pressure without freezing.[5]

Inaccuracies in gauges used for measuring well or field pressures have led to the development of a portable dead-weight pressure gauge. This device, whilst not as convenient as usual Bourdon gauge, proved to be more accurate.[6]

The United States Bureau of Mines has made an extensive study of the problem of corrosion by natural gas which contains H_2S. The results show the influence of pressure, oxygen and moisture on the amount and type of corrosion. In order to reduce corrosion losses in pipe-lines the following should be considered: removal of H_2S, reduction of oxygen content, and control of humidity.[7]

A very simple method of studying the corrosion effect of H_2S on ferrous material has been devised. The natural gas containing H_2S, direct from its source in the field, is allowed to flow over a group of specimens for a given period of time, and an estimate of the amount of corrosion is made from the change in weight.[8]

In addition to the acceleration of corrosion, water vapour in natural gas causes difficulties in measurement and transportation. Solid compounds resembling ice or snow are formed from natural gas hydrocarbons in the presence of water at elevated temperatures and pressures. The formation of these gas hydrates in natural gas lines depends primarily on temperature, pressure and the composition of the gas–water vapour mixture. The formation is accelerated by high gas stream velocities, pressure pulsation, or inoculation with a crystal of the hydrate.[9]

The increasing use and development of automatic gas appliances has made the problem of dust in gas a more serious one, and many companies are studying methods of control. This dust is composed of foreign matter left in the mains, organic material from the gas, material picked up from purification systems, and sand from the wells. The natural gas industry encounters more difficulty from dust than does the manufactured gas industry, because of long transmission mains, high-pressure transmission and the fact that less moisture is present. Dust in gas causes trouble with pumping equipment and compressors, accumulations in meters and sticking of valves and regulators, in addition to difficulties in the operation of industrial and domestic equipment. The trouble has been remedied in part by oil fogging, oil or water scrubbing, filtration or rehydration.[10]

The work on protection of pipe-lines from corrosion has been continued. The economics of pipe-line protection necessitates a study of the condition of the pipe-line, its probable life and the type of protection to be applied if the line is found to be depreciating at an excessive rate.[11] It is believed that future expansion will consist to a large extent in paralleling present lines. The Bureau of Mines has made a study of parallel transmission lines, and has developed several formulas to aid in the design of such systems.[12] A survey of pipe-line transportation of natural gas discusses expansion, length of systems, economics and the question of Federal or State control.[13] The American Gas Association has issued a series of pamphlets on safe practice, the title of one of these being "Safe Practices for Natural Gas Distribution."[14]

In connection with the production of helium from natural gas, the United States Bureau of Mines has developed two new methods of determining the amount of helium in the gas. The first, based on the absorption of the other constituents by activated charcoal at liquid air temperatures, is used for the gas as it flows from the wells.[15] A complete extraction of helium from the natural gas is not practical, and so the gas, when sold to a gas company after this processing, contains some helium. Continuous determination of the helium content of this gas is carried out by a thermal conductivity apparatus.[16]

In a study of natural gases with a view to establishing the most efficient conditions for the extraction of the higher homologues, a method for measuring the dew point of natural gases has been devised.[17]

The Anglo-Persian Oil Company has made a study of the derivatives of

natural gas which are produced by thermal decomposition and polymerization.[18] The experimental work was carried out on Persian natural gas. It was necessary to desulphurize this gas, and this, as well as the pyrolysis, was carried out on a semi-industrial scale. The products were chiefly aromatics, including benzene, toluene, xylene, etc.[19] In a continuation of this investigation a special study was made of the production of styrene and indene.[20]

Natural Gasoline.

The production of natural gasoline continued to decline in 1933, the total output being the lowest since 1926, with a decrease of 7 per cent. from 1932.[21] A reversal of the downward trend which started in 1929 has taken place in 1934. In the first eleven months of 1934 the increase in consumption amounted to 9·8 per cent. over that in a similar period in 1933. It is believed that the low price of the natural gasoline is responsible for much of this increase. There is a tendency towards the use of more volatile gasoline since automobile manufacturers have developed fuel lines which minimize vapour lock. The added anti-knock characteristics of the more volatile blends have also contributed to the development of a better market for this fuel.[22]

Production 1932	1,523,800,000 gals.
,, 1933	1,420,000,000 gals.[21]

The production statistics for 1934 are not yet available.

The problem of corrosion from H_2S in natural gas had already been discussed in connection with natural gas pipe-lines. It is also a problem in natural gasoline plants in such fields as West Texas. When the ordinary type of equipment was used with this "sour gas," difficulties presented themselves immediately. To prevent corrosion special metals and methods of construction were necessary. In one plant seamless aluminium tubes were used in the heat exchangers. It was necessary to make certain parts of the equipment of stainless steel, and other parts had to be made of metal of more than ordinary thickness.[23]

Refrigeration in natural gasoline plants has been a subject of some discussion. The temperature of the absorption oil has an important effect both on the volume of the oil necessary to absorb the gasoline from the gas and on the quality of the gasoline produced. Lower temperatures make the oil more selective. A comparison of refrigerants has been made for the purpose of finding a suitable material for use in the natural gasoline manufacture.[24] One natural gasoline company has recently built a new plant of the compression type, using the principle of gas rectification and utilizing propane for cooling.[25]

Liquefied Petroleum Gases.

The greatest development during 1934 has been in the utilization of liquefied petroleum gases. As a fuel for internal-combustion engines these gases have all the desirable characteristics of gasoline, and possess additional advantages obtainable in no other existing fuel. Very high anti-knock ratings[26] permit the use of high compression ratios.[27] At the present time liquefied petroleum gases are being used extensively by several automobile

manufacturers as fuel in the block testing of their engines. Some utility companies use this fuel for large stationary engines, direct-connected to generators.[28] Tests showed butane to be a satisfactory fuel for tractors.[29] Comparative tests have also been carried out with gasoline and butane on air- and water-cooled aircraft engines.[30]

In areas where this type of fuel is plentiful, transportation companies are investigating its use for their carriers. The Los Angeles Railway system has already adapted eight of its 163 buses to the use of this fuel. This use necessitates an improvement in dispensing systems, and tank trucks are now available for the purpose.[31]

The Southern Pacific Company has carried out development tests for about two years, and has proved to its own satisfaction that butane is a satisfactory fuel.[32] It has now constructed five additional units for operation in Southern California.

An important advantage of butane as a fuel is the absence of noxious odours from the exhaust. This, in addition to economy of fuel and lubrication, makes the use of butane an important development in both rail and bus operation.[31] It is believed that these gases are the ideal fuel for the new high-speed trains.[33] Air conditioning on trains is becoming much more general, and the tendency is towards the installation of mechanical refrigeration rather than ice cooling. Propane will probably prove suited to this type of air conditioning, and, as in the case of the refrigerated truck, may be used both as a fuel and a cooling medium.[34] The many uses for these gases may be shown by the large amounts consumed by two large construction camps. In these camps butane is used for every possible purpose from cooking to running locomotives.[35]

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LIGHT DISTILLATES.

By J. S. Jackson, B.Sc., A.I.C. (Member).

The work carried out during the past year under the above heading has not produced anything of a revolutionary nature, but much sound work has been done, and the existing position has been thoroughly explored and consolidated. On the chemical side, oxidation, spontaneous ignition and gum formation have been extensively explored, and the mechanisms of these processes are now obviously much more clearly understood.

Oxidation.

F. O. Rice [1] has put forward an interesting theory suggesting that in the case of hydrocarbon–oxygen mixtures in engines there may be a preliminary decomposition into lower hydrocarbons resulting mainly from the thermal effect. The increase in the number of molecules increases the rate of oxidation and also the pressure exerted by the mixture. Calculations suggest that there is a parallelism between such decomposition and knocking.

H. A. Beatty and G. Edgar [2] have made an extensive study of vapour-phase oxidation of hydrocarbons, and under stated conditions it was found that, whilst the initial reaction temperature for *n*-heptane was 244° C., *iso*-octane gave only a trace of reaction below 500° C.

P. J. Wiezevich and P. K. Frolich [3] have also investigated the direct oxidation of saturated hydrocarbons at 135 atmospheres pressure and in the temperature range of 300–500° C. in the presence of various catalysts.

An anonymous publication [4] and an article by C. R. Wagner [5] dealt with the use of anti-oxidants in connection with the processing of cracked gasolines. The recommended anti-oxidants are dibenzyl-*p*-aminophenol, monobenzyl-*p*-aminophenol, *p*-hydroxyphenylmorpholine and tributylamine as a colour stabiliser. It is claimed that the anti-oxidant prevents loss in the octane value of the fuel.

Spontaneous Ignition Temperatures.

S. Coffey and T. Birchall,[6] using an S.I.T. apparatus similar to that used by Egerton and Gates, found that for standard gasoline there were two spontaneous ignition zones. Ignition took place between 320° and 335° C., ceased between 335° and 420° C., whilst from 420° C. upwards ignition was continuous. They found that anti-knock substances suppressed the lower ignition zone, whilst pro-knocks extended it. Working along similar lines D. T. A. Townend and L. L. Cohen [7] have shown that true ignition in the lower temperature zone is unusual at atmospheric pressure, but that increase in pressure leads to true ignition. They conclude that knock in an engine is related to the compression ratio adequate to allow spontaneous ignition in the lower temperature zone.

F. J. Dykstra and G. Edgar [8] have also investigated the vapour-phase ignition temperature.

H. F. Coward [9] has described the work of H. B. Dixon on the ignition temperatures of hydrocarbons. He has discussed the inhibiting effects of iodine and organic halides.

Detonation.

A. Egerton and A. R. Ubbelohde [10] have investigated the behaviour of diethyl peroxide in an engine, and have found it to be a violent pro-knock, rather more potent than amyl nitrate. Its knocking action was inhibited by T.E.L. Ethyl hydrogen peroxide was also shown to be definitely a pro-knock. M. Serruys [11] has experimented with a single-cylinder engine in which the air-fuel mixture could be heated to temperatures ranging from 250° to 310° C. He has concluded from his results that peroxides are not the sole cause of detonation, but only constitute a favourable condition.

Lead Tetraethyl.

P. L. Cramer [12] has studied the thermal decomposition of lead tetraethyl in benzine solution, whilst E. Endo [13] has investigated the susceptibility of a number of gasolines and various fractions from the same. They have concluded that the higher members of the sulphur compounds present hinder the action of T.E.L. and are the main cause of the observed selective action of T.E.L.

A very comprehensive survey of the use of T.E.L. in aircraft fuels has been given by F. R. Banks.[14] The conditions which led to the use of T.E.L. are fully discussed. The effects of concentration and temperature on anti-knocks such as benzole and lead are described and compared. The author has dealt in a very informative way with the various troubles which may be encountered in the use of T.E.L. and also with the ways of avoiding such troubles. Such problems as " hot " corrosion of exhaust valves, " cold " corrosion of exhaust valve stems and cylinder bores, corrosion of exhaust pipes and deposit formation of sparking plugs are all discussed in detail. The solutions of these problems by the selection of suitable steels, " stelliting," cooled valves and sparking-plug design are all dealt with at some length. The publication is an important contribution to the literature on the subject.

H. G. Tanner [15] has shown that the addition of T.E.L. to electrolytic hydrogen/oxygen mixture causes an appreciable increase in hydrogen peroxide formation on explosion. This unexpected result is explained and harmonised with modern detonation theories.

The I.G. Farbenind A.-G.[16] have described a method of stabilising T.E.L. The method consists of adding small quantities of sodium, potassium or neutral ammonium fluoride.

Gum.

The mechanism and chemistry of gum formation have attracted a great deal of attention, and much original work has been carried out. It is therefore difficult to summarise the results produced. There have, however, been a number of publications of outstanding merit. J. C. Morrell and collaborators [17] have shown that an increase in the amount of peroxides present in a gasoline results in darkening in colour, increase in gum content, and loss of anti-knock value. These peroxides appear to decrease

the effectiveness of inhibitors, and the response of a cracked gasoline to inhibitors appears to be closely related to the rate of peroxide formation during the induction period. They have investigated the formation of such peroxides in gasoline,[18] and have concluded that the removal of conjugated diolefines and other olefinic hydrocarbons from a gasoline renders the product extremely resistant to oxidation. Diolefines and olefines when present together appear to form more peroxides and gum than when either is present singly in the same concentration. The same workers [19] have studied the mechanism of gum formation, and have concluded that this is closely related to peroxide concentration, and that aldehydes and acids are products of secondary reaction rather than intermediates in gum formation.

E. Vellinger and G. Radulesco [20] have carried out physico-chemical researches on the oxidation of cracked spirit. They have shown that oxygen is essential for gum formation to take place. Such oxidation takes place in the dark, but light accelerates the process, acting as a catalyst. They have found that the amount of gum formed per unit volume of oxygen is greater the higher is the molecular weight of the gum-forming constituents. They have shown that anti-oxidants prolong the induction period, and the efficiency of such inhibitors can be investigated by the photolysis method.

Potassium dichromate has been found effective for the removal of the more readily oxidisable constituents of the cracked spirit which give rise to the formation of peroxides and gum.

T. L. McNamara [21] has discussed in a general way the factors affecting the gum stabilities of gasolines. He has shown that gasoline in contact with air absorbs oxygen slowly during the induction period. In a second stage oxygen absorption proceeds rapidly with considerable increases in gum. The author concluded that exposure to sunlight greatly increased the rate of gum formation, and he has shown that the relative efficiencies of gum inhibitors vary for different gasolines.

P. Woog, J. Givaudon and P. Dacheuz [22] have carried out extensive experiments on the ageing properties of gasolines as measured by " actual " and " potential " gum. The results of the investigation indicated that gasolines containing not more than 10 mgms./100 ml. of " actual " gum gave no trouble in engines.

For the determination of " potential " gum they propose a test involving exposure to ultra-violet light for 1 hr. followed by heating to 100° C. for 3 hrs. in an oxygen bomb.

It has been claimed by A. H. Stevens [23] that gum formation in cracked gasoline can be inhibited by the addition to the fuel of a small amount of an acyl derivative of a polyhydric phenol.

The Universal Oil Products [24] propose to use small quantities of wood tars or their fractions as gum inhibitors, whilst E. W. J. Mardles and W. Helmore [25] claim that urethanes (*i.e.* derivatives of carbamic acid) act as gum inhibitors.

Various.

An exhaust gas analyser is described in the Automobile Engineer.[26] This apparatus depends on the fact that a wire passing an electrical current

takes up a temperature depending principally on the thermal conductivity of the gaseous medium surrounding it.

The behaviour of mercaptans in the presence of copper and mercury has been studied by E. Dittrich.[27] He has concluded that copper cannot be safely used for the estimation of corrosive sulphur.

The articles published by T. A. Boyd [28] and G. G. Brown [29] deal with the vapour-pressure limits proposed by the A.S.T.M. T. A. Boyd considers the limits rather too high, but has shown that 1934 cars show an appreciable improvement as regards vapour lock occurrences. G. G. Brown supports the A.S.T.M. limits, and puts forward the view that the Reid Vapour Pressure at 100° F. is a satisfactory criterion for vapour lock provided the gasoline is tested at the nearest practical point to its ultimate consumption.

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KEROSINE AND WHITE SPIRIT.

By W. H. Thomas, A.R.S.M. (Member).

Kerosine.

Although it does not form the subject of extensive research or of considerable advancements in its utilisation, kerosine still holds its place as one of the most valuable of petroleum products. This is clearly shown in a series of articles which has appeared in the *Moniteur du Pétrole Roumain* [1-10] dealing with petroleum imports into various countries in Europe and the Near East. In Turkey,[1] for example, kerosine is the chief import, whilst in countries as far apart as Holland [2] and Palestine,[6] the consumption of this commodity is quite steady even over a number of years. In a similar connection, the list of world retail prices and taxes on gasoline, kerosine and lubricating oil [11] issued by the United States Department of Commerce is of considerable interest to those concerned with petroleum statistics.

Arising out of the statistical information mentioned above, consideration should be given to the recent standardization of qualities of kerosines. This is exemplified in the U.S. Federal Specifications for Mineral Seal Oil and Long Time Burning Oil,[12] and in Section 173 of the publication of the Japanese Engineering Standards Committee.[13] In addition, French specifications [14] have been issued for kerosine and white spirit, whilst for guidance regarding tax exemption, a United States Tractor Fuel Specification [15] has been adopted by the Western Petroleum Refinery Association. The latter is not in the nature of an official decree.

The A.S.T.M. Methods of Test [16] for kerosine and white spirit have been reissued and in some cases revised, whilst as an adjunct to this well-known annual publication, the same body has recently issued a book [17] on the Significance of Tests for Petroleum Products which devotes a considerable section to the interpretation of kerosine and white spirit tests. It is also of interest to note that the Institution of Petroleum Technologists are catering for a long-felt want in their intention to incorporate in the tests for kerosine a method for the determination of "Smoke Point" and a tentative method for the Burning Test for normal types of kerosine. Methods of test for petroleum products have recently been issued by the Japanese Engineering Standards Committee,[18] and these include tests for kerosine which are listed under the heading of Fuel Oils.

Turning now to the utilisation of kerosine, attention should be directed to Martin's paper [19] to this Institution, dealing with horticultural spray materials, in which the use of kerosine and its refinery by-products, such as sulphonic and naphthenic acids, are mentioned. A patent [20] has been issued specifying a motor fuel consisting of 99 per cent. of kerosine, 0·5 per cent. of ether and 0·5 per cent. of camphor, and Wittka [21] has discussed the interesting possibility of using kerosine in place of alcohol ether, benzene, etc., for laboratory use in tropical climates where volatile solvents are difficult to handle. Kerosine lamps, burners and stoves continue to

receive attention, and a review of the patent literature in this connection indicates that there is still room for improvement in these types of apparatus. Speare and Cooley,[22] in their investigation of a range oil burner, have shown that a satisfactory oil is essential for successful operation. Such an oil should be prepared from a suitable crude, and should be free from high-boiling fractions and corrosive constituents. Improvements in lamps and their fittings have been the subject of a number of patents[23-31]; some of them deal with oil lamps,[23-25] their ventilation,[26, 27] and fume removal,[28] whilst others refer to burners[29] and to wick tubes.[30-31] In closing this section on utilisation, attention is directed to a publication of the Society of Automotive Engineers[32] which gives a broad survey of the question of fuels for tractors; costs, use, properties and demand are fully discussed.

No outstanding work dealing essentially with kerosine has been published during 1934, but the reader is referred to Ellis' recent book[33] entitled "The Chemistry of Petroleum Derivatives." In this, Ellis effectively summarises the refining and reactions of kerosine to heat and various reagents, and enumerates the chemical materials which may be prepared from kerosines of various types. A more limited field has been covered by Critchley in his articles on the refining and testing of petroleum oils.[34] Here, the factors affecting burning qualities are reviewed, the causes of colour reversion are dealt with and a brief survey of modern methods of treatment is given. Another paper of considerable importance to the refiner is that of Thornton,[35] who has described the construction and operation of a continuous counter-current plant which is particularly suitable for the acid treatment of kerosine.

During 1934 an appreciable number of patents was issued dealing with methods of treatment suitable for the refining of kerosine. New sweetening processes have been suggested,[36-43] the reagents being of diverse nature; some of the processes are variations of the well-known doctor treatment,[36-40] and others specify the use of oxidising agents such as hydrogen and sodium peroxide,[37, 41] whilst in some patents[42, 43] cupric sulphate and brucite are specified. An equal diversity of reagents[44-55] has been suggested for the desulphurisation of light distillates such as kerosine. Various types of alkali treatment are covered by six patents,[44-49] other suggested reagents being dry calcium hypochlorite,[50] aluminium chloride,[51] ketones,[52, 53] brucite,[54] and halogens operative in the presence of catalysts.[55] Hydrogenation, followed by solvent extraction for the removal of aromatic and unsaturated hydrocarbons, has been suggested as a means for refining burning oil in two patents,[56, 57] and one by Egloff[58] specifies treatment with hydrogen at an elevated temperature in the presence of phosgene while in contact with charcoal. Clark[59] claims that an improved kerosine may be produced from unrefined distillates by hydrogenation, the reaction being controlled so as to limit the formation of motor spirit, whilst Aleksandrov,[60] dealing with the destructive hydrogenation of Grozny oil, has given details of autoclave treatment of kerosine in the presence of iron and nickel catalysts. Turning now to the acid treatment of kerosine, there is a paper by Virdyantz[61] on the separation of aromatic hydrocarbons by means of 97–99 per cent. acid which deserves mention, and three patents[62-64] dealing with variations in normal types of acid refining have been issued. Others[64-69] concern the neutralisation of acid-treated oil, the reagents used being

silica, sodium hydroxide, magnesium hydroxide and powdered dolomite. Two patents [70, 71] on the solvent extraction of kerosine have appeared, and the Burmah Oil Co.[72] specifies the use of a mixture of bauxite and aluminium sulphate as a refining medium. Of a miscellaneous nature are papers on the corrosion of metals by kerosine [73] and on the thermal decomposition of this material.[74] The former deals with the effects of Ural and Baku kerosines on lead, brass, copper, iron and aluminium, and the interesting fact is stated that kerosine saturated with water attacks metals more readily than when dry. The latter paper is an account of laboratory investigation, the materials dealt with being obtained from Moreni crude petroleum.

Kerosine as a source of naphthenic acids has continued to receive attention. In a series of articles by Pyhala[75–77] on the presence of naphthenic acids in kerosine it has been shown that the complexes, which mask the presence of these acids, break up during distillation or acid treatment and set free the acids. The utilization of these acids in the form of soaps has been described in papers [78, 79] dealing with the application of kerosine and naphthenic acid soaps for the production of insecticides.

White Spirit.

Comparatively speaking, there is little to comment upon with regard to white spirit, very few outstanding papers on this subject having been published during 1934. Perhaps the most interesting is that by Sweeny and Tilton,[80] who have given data on the properties of hydrogenated solvent naphtha and its fractions, the starting material being sulphur dioxide extract from kerosine. Two anonymous articles, one on the relative merits of white spirit and chloro-hydrocarbons,[81] and the other on paint driers,[82] have been published, and two patents, one by Reid [83] dealing with apparatus for the acid treatment of cleaning solvents, and the second [84] covering the recovery of solvents from alkaline sludge, have been issued.

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LUBRICANTS AND LUBRICATION.

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The past year has seen the real advent of specific solvent extraction processes for the refining of lubricating oils. Presaged by the preliminary successes of the sulphur dioxide and phenol methods of treatment, the big advances anticipated for processes involving the use of propane in combination with other solvents are being well realised. Solvent extraction as a whole may be considered the biggest advance in the refining of mineral lubricating oils since the development of vacuum distillation. Not only are the final products vastly improved in all the qualities sought and still being sought, but the basis of supply has been broadened. Far more crude oils may now reasonably be looked upon as natural sources of lubricating fractions. Indeed, decisions in that direction have already become matters of economics rather than technology. For this reason, a review of the situation by Wilson and Keith [1] from the aspect of economics has particular interest. It is not possible in a summary to do justice to this reasoned presentation. It is noteworthy, however, that Wilson and Keith predict that the additional cost of solvent treatment and dewaxing, combined with comparatively low yield, will not justify attempts to make oils of really good viscosity index from asphaltic base crudes. Nevertheless, the oxidation and coking properties can be substantially improved by limited processing; the products may then be diverted to industrial purposes where viscosity index is of less importance. On the other hand, the cost of producing lubricants corresponding to present Pennsylvanian types from Mid-Continent crude oils will not prove prohibitive. In this case not only is actual yield better, but it also becomes of less relative significance, owing to the total amount processed being greater than requirements. Yield is then only of importance in affecting the cost of operation. The future of the paraffinic base oils may be gauged from the fact that by solvent refining, and with only comparatively small loss, such stocks can be made to yield oils up to 115 Viscosity Index. This may be a means of maintaining their traditionally high position.

The importance and use of propane as a refining agent continue to be recognised and extended. Bray, Swift and Carr [2] summarise the application of this liquefied hydrocarbon as follows:

(*a*) To deasphaltise asphaltic or mixed base crudes.
(*b*) To dewax residual or distillate oils.
(*c*) As one of a combination of selective solvents.
(*d*) As a diluent in clay and acid treatment.

Its most important features are doubtless the readiness with which it can effect removal of asphalt and the easy filtration of wax from its solutions following temperature reduction on partial evaporation. Conine,[3] indeed, reports Keith as describing the continuous processing of Pennsylvanian oils with propane to give a drop in pour point of more than 80° F.

At the same time, although there is no asphalt to remove, a segregation occurs of resins having high coke values which in practice permits the use of higher viscosity residuum and use of a larger proportion of neutrals.

In actual practice the use of propane is probably most closely identified with the Duo-Sol or Clearosol processes,[4] plants for the operation of which are now well into action. The simultaneous use of two solvents permits variations in the quantity of each solvent and of the solvent ratio sufficient to cope efficiently with any suitable raw material and for any chosen product obtainable.

The growing importance of propane in refining lends particular colour to an interesting paper by Goddewicz and Pilat,[5] describing fractionation of petroleum by means of hydrocarbon gases dissolved under pressure. Cold fractionated lubricating oils obtained by this method give far superior viscosity indices than corresponding oils obtained by distillation. This work is based upon, and appositely refers to, the Polish patent of the Institute for Chemical Research of as far back as 1920, describing the use for fractionating purposes of hydrocarbons boiling below room temperature.

Theoretical and process aspects of solvent extraction refinery operation have been dealt with by Evans [6] and by Waterman, Kruijff, Schönlau and Tulleners.[7] Examining the problem from a physico-chemical point of view, the former develops methods, mostly graphical, for following and dealing with the conditions arising from partial or non-miscibility and batch or counterflow extraction. This paper is worthy of examination by those interested. The latter authors describe the use of refractive index combined with other properties for following sulphur dioxide extraction of lubricating oils; but the method is obviously of interest for all other specific solvent separations.

The proved success of solvent extraction has brought forth a spate of processes and patents, of which the claims for trimethylene [8] for the purpose of differentiating between polar and non-polar compounds, of furfural in amylamine, of crotonaldehyde and acrolein appear the most interesting.

It is apparent that the use of Paraflow for depressing the pour point of lubricating oils [9] is now well-established practice. Here again imitation has proved the sincerest form of flattery. This may be judged from the numerous patent [10] and other claims for the discovery of products of similar properties; as, for example, distearylnaphthalene and the myricyl ethers of the oxynaphthalenes.[11] As a theory of the action of such materials, Zimmer, Davis and Frolich [12] suggest that they are adsorbed on the surface of the wax particles, thereby preventing the growth of the latter and at the same time their capacity to adsorb oil and form gels. The oil thus moves freely, although the solid wax particles continue to be suspended within it.

Despite the progress made in the improvement of mineral lubricants from natural sources, much attention continues to be directed towards the synthesis of hydrocarbons having lubricating properties. Judging by the published work of investigators of standing and by patents granted in various countries, a fair measure of success has been achieved. The raw materials in most cases are olefines, but Atkinson and Storch [13] point out that the lower molecular weight members of this series polymerise to oils of poor viscosity index. With increasing length of the carbon chain,

however, lubricating properties improve. By polymerizing ethylene successively thermally to a liquid and thereafter by aluminium chloride, really good viscous oils are obtained having Viscosity Indices running from 58 to 108. Schildewächter [14] also continues his work on ethylene condensations, and obtains oils of good viscosity, free from asphalt or tendency to asphaltize, by using naphthalene and its derivatives. Of the large number of patents on the subject, those of Osterstrom [15] are of special interest because of their association with vapour-phase cracking, whence viscous polymerization products may be obtained by suitable operation of the process. The oils,[16] by the way, are themselves alleged to effect removal of wax from solvent diluted distillates. Similar claims to those of Osterstrom in regard to vapour-phase cracking have been made elsewhere,[17] and it certainly seems reasonable to look to this source, if anywhere, for a sufficient supply of labile hydrocarbons for the synthesis of lubricants.

Of a different though related type is the work of Fischer and his colleagues,[18] referred to in previous Reports, on the production of synthetic lubricants from Kogasin, itself the synthetic product obtained from carbon monoxide and hydrogen. The oils thus obtained continue to improve in character, those from the condensation of chlorinated Kogasin with aromatic hydrocarbons being especially well reported on. At the same time, their method of production gives food for thought on the possible general constitution of the natural lubricant hydrocarbons. In the latter connection, Washburn [19] described the work being carried out by the A.P.I. on the isolation and identification of individual hydrocarbons from lubricating oils with a view to the attempted synthesis of related compounds of identical empirical formulas. Because of its origin, mention is made of a patent claim [20] of the I.G. to produce lubricants by the action of high-frequency electric discharge on paraffin wax.

Turning to the chief properties of lubricants, it is natural that most of the work on viscosity has been concerned with expression of viscosity index and viscosity–temperature relations. Grosholz [21] and Watson [22] have prepared charts for the comparison of oils on a viscosity index basis, the latter presenting a method for reading Dean and Davis V.I. direct from any two viscosity measurements within the range. Docksey, Hands and Hayward [23] have prepared useful Viscosity Index Charts (Dean and Davis Index) using the reference temperatures employed in the United Kingdom and on the Continent. Viscosities over a wide range are expressed in centistokes. In general, these authors agree with the accuracy of the A.S.T.M. viscosity–temperature chart, but point out that much greater accuracy in obtaining individual points on the viscosity–temperature line is reached, instead of by drawing, by use of the equation log. log. (centistokes $+ 0{\cdot}8$) = A log T + B. Alberheim, Konheim and Larson,[24] on the other hand, state that at low temperatures the A.S.T.M. chart is not strictly accurate, and suggest for the ordinate scale log. log. (centistokes $+ 1{\cdot}22$).

No marked steps have been taken during the year towards the desirable goal of international standardization of measurement or expression of viscosity. Fenske and McClure,[25] in entering a plea for the determination and expression of viscosities in fundamental units, point out that such results can be transposed to conventional scale units for commercial purposes as long as is required. They also describe a modified Ostwald apparatus

suitable for rapid measurements repeatable to within 0·2 per cent., and wherewith it is possible to average forty determinations a day.

Most of the published work on oiliness has been in connection with considerations of the theory of boundary lubrication. Bridgeman,[26] however, has done some interesting work with practical possibilities for direct comparison of the lubricity of oils by observing their behaviour in bearings at low speeds. The effect of temperature on lubricity is stated to be considerable. This fact may have some bearing on the reasons for the continued attempts to ascribe the property of oiliness to particular constituents even in natural petroleum lubricants. Wardner[27] concludes that such materials, which he terms "proto-oil," are dispersed in the inert remainder. By fractional extraction with acetone he actually separated a small quantity of a material very unctuous in properties and of high molecular weight. Rhodes and (A. W.) Lewis[28] appear to have gone farther in a parallel direction, for they allege that certain new types of substances in very small quantities, notably β-naphthol, are effective in increasing oiliness. This, they say, is by virtue of such compounds acting as negative catalysts to the oxidation of the oil. From measurements of static friction in bearings they conclude that the adsorbed layer effecting oiliness is formed slowly, but, once formed, cannot be removed without destroying the active constituents.

A study by Nottage[29] of the boundary lubricating value of mineral oils of different origin has been published by the Department of Scientific and Industrial Research as a separate Technical Paper No. 2. From this work it appears that oils may have abnormal properties at a solid interface, and that it is such behaviour, due possibly to selective concentration, which may determine their value. Nottage also points out that in certain conditions wax may be an advantage rather than a hindrance in a lubricating oil.

In view of other recent work on oxidation, it is interesting to note that Rhodes and Lewis[30] affirm these active constituents to be destroyed at temperatures above 75° C. An outstanding publication of the year was that of R. O. King,[31] wherein he summarized much of his previous investigations[32] into the beneficial effect of oxidation on the lubricating properties of mineral oils. King's work is concerned primarily with high-temperature lubrication, and his measurements are directed towards the observation of seizing temperatures on the lines originally indicated by Stanton. Whether or not seizing temperatures are measures of lubricity in the sense of the Herschel definition, may be uncertain. It is apparent, however, that they represent actual lubricating value under certain conditions. Observations that by drastic atmospheric oxidation an ordinary oil may reach a seizing temperature of 309° with a minimum coefficient of friction of 0·0005, are therefore of considerable importance, and likely to have far-reaching results. Without being in a position to propound a fully satisfying theory of lubrication therefrom, King cogently points out the more-than-coincidence that Hardy had already shown how oils from which the polar constituents had been partly removed could be re-activated by air even at ordinary temperatures. A forthcoming oxidation theory of lubrication is therefore likely. Straight oils of varying types behave very differently as regards oxidation lubrication, and all, even the best, the Pennsylvanian oils, can be improved by blending to obtain maximum lubricating value.

In the recently issued report[33] of the Department of Scientific and Industrial Research for 1933–1934, reference is made to the continued work with the Air Ministry on the oxidation of oils in relationship to their seizing temperatures. It is indicated that maintainable optimum surface conditions may be produced by comparatively slight oxidation.

Whilst attention has been focussed by King's work on the apparent desirability under certain conditions of a modicum of oxidizability, the disadvantages of excessive oxidation on lubricating oils are too well known to be minimized thereby. Because of their subsequent appearance on the market, it is well, therefore, to refer again[34] to the inhibitor-treated oils of Helmore and Mardles. The latter,[35] describing the use of tin as an anti-oxidant, states that the effects vary with the compound of tin used, its concentration, the nature of the oil and other conditions. It is claimed that by suitable application there is achieved less sludging, lower viscosity increase, less gum deposit and in general a longer life. Amongst the most effective tin compounds are fatty acid salts, phenates and naphthenates; and certain organo-metallic compounds.

Considering its importance to industry as a whole, astonishingly little published work has appeared on the fundamental aspects of lubricating (and insulating) oil oxidation. Klatt[36] has initiated researches on the air oxidation of partly cracked oil with a view to determining the incidence and nature of the products. Boisselet and Mouratoff,[37] also working on the nature of the products, find that when using oxygen the acidic products can be partly identified, or at any rate classified. The lower molecular weight compounds may be quite simple acids like acetic and formic, whereas the higher are simple saturated cyclic acids with additional oxygen in the ring structure. Otherwise there is very little; and that mostly to do with the development of oxidation tests which are not strictly in place in this sectional report. Reference must be made nevertheless to an investigation by Chebotar[38] into the oxidation of transformer oils as measured by the rate of absorption of oxygen at 300 lb. pressure. By this means it is possible to show that all oils pass through an induction period, after which there is a rapid acceleration in oxidation, followed by a marked slowing up. It is noteworthy that in actual tests there is a tendency to copy the British Air Ministry methods, *e.g.* in the Indiana test[39] and by Guthrie, Higgins and Morgan.[40] These are mentioned chiefly because it is clearly stated by their sponsors that they are not claimed to be measures of behaviour in service, but merely means of supplementing practical observations. Fischer and Marinoff[41] consider that light translucency may be a measure of stability, and hence of durability in service. They reach other interesting conclusions from much work on thin films absorbed on filter paper, but the basis of the investigation is obscure.

Barnard, Barnard, Rogers, Shoemaker and Wilkin[42] have closely surveyed the factors contributing to sludge formation in motor oils. Many bench tests were correlated with analytical results and the conclusion was reached that the asphaltenes from the oxidation of the oil are the clue to the sludgy deposits. The authors claim to be able almost exactly to predict the course of asphaltene formation in the engine. Otto, Miller, Blackwood and Davis[43] also analyse the operating conditions in a modern motor, and come to the conclusion that oils of Viscosity Index 120 and

above are needed. These not being ordinarily obtainable so-called *iso*-paraffinic compounds have been brought into use as dopes. These substances, termed "Exanols," obtained by the polymerisation of refinery light ends, are stated strikingly to increase viscosity index when mixed with lubricating oils even in small proportions.

The question of extreme pressure lubricants continues to attract a great deal of attention. Bridgeman [44] reports the progress made by the U.S. Bureau of Standards since they started to investigate suitable tests for these materials. Probably the best of the testing machines available is the Timken tester, descriptions of which are readily available.[45] The Bureau is stated nevertheless to be developing its own machine, and to be prepared to despatch duplicates for co-operative work to different laboratories interested in similar investigation. Mougey,[46] in discussing the nature of E.P. lubrication, considers it to be a function both of the lubricant and the metallic surface. The sulphur, chlorine or other ingredient is believed actually to enter into combination with the bearing surface, and hence to be more effective if free or present as a reactive compound. For this reason, lead soaps are considered to take some time to build up their E.P. film. These E.P. lubricants originated chiefly to meet the needs of the automotive industry. They are reviewed in a paper by Wilch.[47] In a fine general description of lubricating greases, Garlick [48] also devotes considerable space to the lead soap greases and their manufacture. No patents appear to have been taken out for E.P. lubricants during the past year. Most of the extensive patent literature on lubricants is concerned with methods of cleaning or recovery, of dewaxing, of solvent extraction or synthesis. Beyond those mentioned previously, few seem to call for special description or reference, although Craik and I.C.I.[49] record in their patent that gel-type thickened oils may be obtainable by using cellulose esters such as the palmitate or stearate.

Of more than passing interest to the oil industry has been the publication of a report by the Manchester Committee on Cancer.[50] This report summarizes the Committee's conclusions and offers a standard for spindle oils based on an alleged relationship between carcinogenicity in mice and refractivity and specific gravity of the oil. Whether such far-reaching conclusions will go unchallenged remains to be seen. A paper by Woodhouse [51] on the carcinogenicity of oils is of interest in showing by mouse tests that a synthetic oil prepared from ethylene had no cancer-producing properties. In the case of a sulphur-dioxide-treated oil the carcinogenic constituents were found to be concentrated in the SO_2 extracts.

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GAS OIL, FUEL OIL, ETC.

By Walter A. Woodrow, A.I.C., F.C.S. (Member).

Diesel Fuels.

A paper by Rothrock [1, 67] states that photographs of an N.A.C.A. compression ignition engine fitted with a 2·5-in. glass window shows that with a short ignition lag, the flame starts at the surface of the spray envelope, but with a long ignition delay, burning may commence at any point in the chamber. Sass [2] suggests that the ease or retardation of ignition depends more on the molecular chemical structure of a fuel than in the physical properties. According to Boerlage and Van Dyck,[3, 68] active oxygen and activated hydrocarbons both influence self-ignition in Diesel engines, and a low thermal stability is necessary for a high oxidation speed : these authors have also correlated the condition of cracking with the behaviour of fuels in an engine. A paper by Schmidt and Gaupp [4] indicates that vegetable oils can be used in Diesel engines, but with a lower efficiency and higher consumption than gas oil. A comprehensive survey of the ignition properties of Diesel fuels has been given in a paper by Moore and Kaye.[5] These authors have correlated ignition delay with cetene number and shown that there is a relationship between the cetene number of a fuel and its viscosity–gravity constant as determined by a modification of the Hills and Coats method.[6] A useful table is given in the paper,[5] which the authors suggest can be used in conjunction with the specific gravity and viscosity of a fuel to predict the ignition qualities. Le Mesurier and Stansfield [7] suggest that ignition quality of fuels can be measured by two methods : (*a*) by measuring the delay angle, *i.e.* degrees of crank movement between injection and commencement of rapid pressure rise, (*b*) the inlet air to be progressively throttled until a point is reached at which the fuel will not fire when injected : these authors also suggest that when no test engine is available the aniline point could be used, which is stated to be reliable except with some abnormal and doped fuels. Becker and Fischer [8] find there to be a correlation between critical compression ratio (C.C.R.) and a function of the aniline point and specific gravity. These authors propose for this function to be a " Diesel Index " of ignition and combustion characteristics of fuel oils and to be defined as Diesel Index = Aniline Point (° F.) × A.P.I. gravity/100. The Diesel Index decreases as the C.C.R. increases, the latter varying as the logarithm of the former. A fuel oil for use in compression ignition engines is suggested by Howes [9] in which is dissolved up to 10 per cent. of an aliphatic or aromatic diketone, *e.g.* acetyl acetone or benzoyl acetone to reduce the S.I.T. Rendel [10] states that the delay period for fuels for Diesel engines should be as short as possible; the ignition quality, which is dependent on chemical structure, can only be determined by an engine test. Viscosity should not be too low, to avoid leakage past fuel pumps and plungers; on the other hand, a fuel should not be too viscous, because suitable means of heating are not provided in automotive equipment.

Incomplete combustion gives rise to dirty exhaust and sticking of piston rings. Corrosion troubles due to sulphur are unimportant, and if corrosion occurs in exhaust lines, lagging should overcome this difficulty. To shorten the delay period of a fuel, Howes [11] adds not more than 2 per cent. of an alkyl nitrate and 0·1 per cent. of an organic bromine or oxygenated copper compound, and as a primer for a fuel Howes,[12] in a patent, claims that NO derivatives of an aliphatic or heterocyclic compound free from aromatic groups are suitable. It is suggested [13] that the product of distillation of oleaginous grains or peanuts can be used alone or in mixture with gas oil or shale oil. An anonymous article [14] states that at present only one-third of the available gas oil is suitable for Diesel fuel owing to the low cetene number of the remainder; the amount of potential Diesel fuel in the form of P.D. Bottoms is increasing, indicating the necessity of adapting the Diesel engine to use these low-grade fuels which are at present unsuitable. Le Mesurier and Stansfield [15] state that all fuel oils collect abrasive material, and suggest that this should be removed from the oil as near to the service tanks as possible; they also state that formation of nozzle carbon is determined by engine design, degree of cooling and position of spray nozzle. Corrosion of crank-pins is not due to sulphur content, but to the amount of free HCl (from sea water) present and to the size of the acid/water droplets dispersed through the oil. A Diesel fuel to the amount of 44–55 lb. per ton of coal is produced by the Kopperskohle [16] process. The A.S.T.M. Standards [17] on Petroleum Products contains a classification of types of fuel oils suitable for use in Diesel type engines. This classification, covering five grades of oil, was developed by Technical Committee D-2 on Petroleum Products. The feature of ignition quality is included and is considered under (1) Diesel Index, (2) Cetene number, which is the percentage of cetene in a blend of cetene and α-methylnaphthalene, which has the same ignition quality (measured in a specified engine under a definite set of engine conditions) as the fuel under test, (3) Critical Compression Ratio, which is determined on a C.F.R. engine modified to run as a Diesel engine. The critical compression ratio is obtained by motoring the engine at a selected speed and noting the compression ratio at which firing occurs (as judged by the sound of the exhaust) within three seconds after the fuel is injected. It is stated that none of these methods has been sufficiently correlated with service performance to justify setting definite limits. The methods relating to ignition quality are not considered practicable for determining ignition quality of grades 5–D and 6–D mentioned in the above classification.

Oils for Carburetting Purposes, Wash Oils, etc.

Schläpfer [18] has reviewed the carburetted water-gas practice in Switzerland. The adsorptive capacity of wash oils has been investigated by Leroux,[19] who passed dried nitrogen through wash-bottles of previously prepared gas oil containing benzene, finally absorbing the benzene in a mixture of 98–99 per cent. sulphuric acid containing 3 per cent. silver sulphate. A patent by Hickney [20] describes the preparation of permanent gas from fuel oil by intermixing in vapour form with a catalyst such as firebrick with one of several metallic oxides. Morgan and Stolzenbach [21] have examined heavy oil–tar emulsions from carburetted blue gas plants

under the microscope using nitrobenzene as a solvent. Schumacher [22] produces carburetted water-gas by introducing tar or oil mixed with steam on to the top of the charge during the last few hours of carbonisation; he discusses the relative position of the oil sprays and off-take pipes in relation to the use of the process in vertical, inclined or horizontal retorts. Schuster [23] has reviewed previous work dealing with the relation of the chemical constitution of oils to their ease of cracking and gas-making properties. A patent by Hall [24] deals with the carburetting of water gas by spraying a heavy oil or residuum on to the surface of the fuel bed in the generator during the steam-up run; during the following air-blasting operation, additional air is supplied marginally to the top of the fuel-bed, and is also injected under pressure on to the central position of the fuel-bed surface. Oil residues deposited thereon are thereby consumed, and clogging of the surface is avoided. Rosier [25] gasifies oil in the presence of a catalyst, heats it further, and then injects air which has been separately preheated into the oil vapour. A patent by Stone [26] covers the use of heavy oil in the manufacture of carburetted water gas. Elliott and Huff [27] have experimented with Bunker C oil by cracking on a refractory surface of magnesia blocks in the presence of steam at 704–871° C. They found that impregnation of the blocks with 5 per cent. by weight of sodium carbonate greatly accelerated the steam-carbon reaction at 871° C. as compared with unimpregnated blocks, but this acceleration became less as the temperature fell to 704° C. More carbon appears in the form of blue gas, and less is present in the impregnated surfaces. There were no indications that Na_2CO_3 had any effect on the pyrolysis of the oil. Ditto,[28] in a patent, deals with the production of fixed combustible hydrocarbon gas from a mixture of heavy hydrocarbon oil and water which has been preheated with air to aerate the liquids to an extent of 10–25 per cent. increase in volume. The mixture is homogenised and emulsified, and finally subjected to sufficient heat to produce a fixed combustible gas. Kopelevich [29] has compared the benzene absorption abilities of gas oil and coal tar oils; he finds that in the determination of the vapour pressure of benzene in these oils Henry's law does not hold. A patent by Perry [30] deals with the use of heavy oil in the manufacture of carburetted water-gas. Blast gases are burned in a vessel of refractory material to establish a path of radiant heat over which blue water-gas passes, which is then carburetted with heavy oil.

Heavy Fuels.

Dunlop [31] summarises the details of the Admiralty trials and specifications for fuel oils satisfactory for naval use, and states that coal/oil fuel mixtures are unsuitable for modern warships. Colloidal fuels have received a fair amount of attention, as the following references will indicate. An English patent [32] states that coal/oil mixture can be made by mixing coal and oil with a gelatiniser and a small proportion of wool pitch, wool fat or vaseline. A patent by Tod [33] describes a furnace fuel consisting of fuel oil and pulverised coal or coke, together with cork flour or ground cork bark. Dispersions of coal in oil [34] (rich in aromatic, naphthenic or asphaltic constituents) can be produced by agitating the two materials with not less than 5 per cent. of a non-aqueous peptising agent at 300–370° C. and at 50

atmospheres pressure. Wyndham [35] produces coal/oil mixtures by passing the components through a mill comprising co-acting rollers, positively driven in opposite directions at different peripheral speeds. Another coal/oil fuel [36] is produced by stabilising the mixture with 0·1–2·5 per cent. of paraffin wax, ozokerite or stearic acid, and then treating with about 1 per cent. of ammonia, whereby the tendency to set on cooling is inhibited. Nesfield [37] claims to produce a stable suspension of coal in oil by means of a specially constructed mixing plant. Roberts [38] uses starch as a stabiliser for coal/oil mixtures, and adds sodium chloride and boric acid as combustion-promoting agents. In a patent by Wyndham [39] suspensions containing up to 70 per cent. of coal in oil are described. A Japanese patent [40] states that the work done by a fuel oil is increased by adding about 30 gms. of the following mixture to 5 gallons of fuel oil; 100 parts naphthalene, 5–10 parts anthracene and 1–3 parts phenanthrene. Hamilton [41] suggests that fuel oils be bought on the following basis: Bunker A—20° A.P.I., Bunker B—15° A.P.I., and Bunker C—10° A.P.I. with 0·3 per cent. of the price subtracted for each degree above 21°, 16° or 11°, or 0·3 per cent. added for each degree below 19°, 14° or 9° respectively.

Gentil [42] has dealt with the uses of heavy fuel oil, gas oil and tar oils for marine and Diesel purposes. A patent by Stevens [43] covers a process for reclaiming fuel oil from sludge deposited in storage tanks. Klees [44] avoids oxidation, *e.g.* of steel at high temperatures, by atomising the preheated liquid fuel into a portion of flue gases at below the cracking temperature to obtain a gas mixture of 200–2000 B.Th.U. per cu. ft. This gas mixture is burned with preheated air in a chamber free from abrupt changes of section. Haylett [45] takes heavy low-grade fuel oil, which he distils at its incipient cracking temperature, whereby 25–30 per cent. of gas oil is obtained. The residue is cracked to produce up to 10 per cent. gasoline and a cracked oil of similar characteristics to the original but of lower specific gravity. In a paper dealing with the calculation of the heating value of fuels from their elementary analysis, Schuster [46] has devised three new formulæ employing both linear and quadratic relations of the calorific value/air demand function. Grant [47] has designed the "DX" fuel-oil burner of variable output, this variation of output being achieved by alteration of the oil supply. Trials made with two boilers in parallel with steam consumption of 38 tons of steam per hour showed that it was possible to vary the steam pressure of the one fitted with "DX" burners between 10 and 31 tons per hour without extinguishing any of the burners, but to maintain similar results on the other boiler fitted with ordinary burners required six out of seven burners to be extinguished. A patent by Oppenheim [48] deals with a process for using heavy oils in internal-combustion engines by means of a body of heated activated carbon catalyst, arranged to interconnect the carburettor and intake of the engine. An article [49] by an Italian technical committee quotes the details and precautions to be taken when sampling fuel oil tanks: it is recommended that the size of the sample should be usually 0·1 per cent. of the quantity to be sampled. A paper by Damany [50] gives a formula for calculating calorific value—namely, calorific value = 8·133 C + 29·15 H, which is the upper calorific value expressed in Cal. It is stated that values agreeing within 0·1–0·6 per cent. of actual determinations are obtained in the case of fuel oils. Damany obtains the lower calorific

value by subtracting from the upper calorific value the heat required to raise the water formed from 15° to 100° and convert it into vapour, this being given by: upper calorific value—55·9 H. In a paper by Gurley and O'Niell [51] dealing with the tendency of cracked fuels to form deposits in fuel oil heaters in naval service, one of several tests described is the use of a Sharples super centrifuge, through which is passed one gallon of a sample at 30,000 r.p.m. Examination of fourteen different oils revealed that there are one or two distinct types of sediment, (1) a comparatively dry carbonaceous sediment, and (2) a sticky gummy sediment. It was found that oils containing the latter type of sediment showed a greater tendency to form heater deposits than oils containing the former type. Another distinction between the composition of these deposits is that those which appear carbonaceous contain a lower percentage of water-soluble sulphates than those which appear sticky, and a table given indicates that heater deposits increase with the increase in percentage of water-soluble sulphates. Brierly [52] states that the optimum viscosity for fuel oil to the burners is 150 seconds Saybolt Universal for cracked and non-cracked fuel oils. He found that certain types of cracked fuels do produce excessive deposits of carbonaceous material in storage tanks, lines, strainers and atomisers of fuel oil heaters. He concludes that losses with carbonaceous material in the stack gases are at a minimum when viscosities of fuel oils to the burners are about 150 seconds Saybolt Universal, and he also states that furnace temperatures, burner arrangements and flame conditions are highly qualifying factors. The use of cracked fuels does not cause greater slagging of brickwork than non-cracked fuel oils, unless ash content is abnormally high. Slagging is a function of the character of the ash and its amount. Referring to cracked fuel oils, Becker [53] states that when heating fuel oil to obtain proper atomisation, it is essential to maintain what is known as the viscosity-flash relationship; that is, the temperature at which the oil has a viscosity low enough to permit good atomisation must be at least 20–40° F. lower than the flash point, otherwise coking in the heating coils may occur. A paper by Borgstrom, Norton and Lewis [54] describes at length hydrogen-carbon/ratio (H/C) of fuel oils, which is obtained by dividing the percentage of carbon by 12 and the percentage of hydrogen by 1·008, and then dividing the value for the carbon into that for the hydrogen. For aliphatic hydrocarbons of the paraffin series, this H/C ratio is slightly higher than 2, depending on the length of the carbon chain, whilst for the aromatic series it is unity or less. It is stated that the H/C ratio increases as the specific gravity decreases, and oils with a ratio of less than 1·5 are cracked residues or blends, whereas straight-run residues have a ratio of 1·77–1·56. These authors suggest that the H/C ratio can be used as an aid to identification of the treatment a fuel oil has received during production, and, further, that the viscosity and specific gravity in conjunction with the H/C ratio will aid in the identification of the kind of charging stock used. Rather [55] considers that properly processed cracked fuel oils of the present day are to be preferred; they are higher in calorific value than virgin products gallon for gallon, and generally have comparatively superior viscosity–temperature relationships. McGeary,[56] dealing with fuel oil specifications for the U.S. Navy, discusses ash content: he says that although it is known that ash is detrimental to the brickwork in the boiler, it has not been definitely deter-

mined whether it is the quantity or character of the ash which has to be guarded against. He suggests that an ash content of 0·10 per cent. which contains 80 per cent. of salts may be, and probably is, more destructive to brickwork than an ash content of 0·4 per cent. which contains only 10 per cent. of salts. He further suggests it may eventually be necessary to limit both the total ash and the destructive salts.

Miscellaneous Fuels.

Trials have been made in Belfast [57] with standard vehicles using redistilled light creosote as fuel, but although higher compression ratios can be used, these trials have been discontinued owing to many disadvantages. Tar oils are apparently a success for stationary spark ignition engines, but quite unsuitable for compression ignition engines because of their high S.I.T. An article [58] in the *Fuel Economist* contains agreed conclusions regarding the use of compressed gas for motor transport. Halliwell [59] describes the difficulties experienced in converting a vehicle having a compression ratio of 4·45 to 1 from petrol to town gas; he states that correct adjustment of the reducing valve was of the utmost importance. A simple gas producer for use on vehicles is described in *Engineering*.[60] A stable water-in-oil emulsion to be used as fuel is described in a patent by Vance,[61] who subjects an intimate 2 : 3 mixture or water and crude petroleum to a pressure greater than 7000 lb. per square inch at 37° C. Adams [62] mixes coal tar with a cracked fuel oil having a fixed carbon content of < 5 per cent. producing a stable fuel which gives no deposits on keeping. As a means for permitting the use of heavy fuel oils for engines, Oppenheim [63] renders the fuel more inflammable by passing it over a heated catalyst mass prior to entering the carburettor. Russell [64] deals with the combustion of oil/water emulsions. Lubovitch [65] claims improvements in the combustion of solid or liquid fuels by the addition of a mixture of salts or oxides of the rare earths and/or of barium together with an alkali chloride. Trials have been made in London [66] with a Koela producer gas plant fitted to a vehicle. Charcoal or coke may be used as fuel, 12–15 lb. being equivalent to one gallon of petrol.

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ASPHALTS AND ROAD MATERIALS.

By A. Osborn (Associate Member).

General.

The consumption of asphaltic bitumen in 1933 was much the same as in the previous year, according to figures given by Schmidt [1] for production, import, export, and consumption of bitumen throughout the world, and although it is interesting to note that Great Britain produced 11·8 per cent. of the world's total production as compared with 8·4 per cent. in 1932, the actual amount for 1933 was only 345,000 tonnes, whereas the amount produced in 1932 was 382,000 tonnes. This increase in the percentage was due principally to decreased production in the United States, which, however, still heads the list of countries producing bitumen with 65·6 per cent. of the total production. Germany comes third with an actual increase of from 266,000 tonnes in 1932 to 336,000 tonnes in 1933, while France is fourth also with an increase of from 123,000 tonnes in 1932 to 167,000 tonnes in 1933. These four countries thus account for 88·1 per cent. of the world production.

Figures for production of rock and natural asphalt in 1933 and for consumption over the period covered are not given, but a decrease in the use of these materials is indicated by the statistics relating to import and export by various countries.

According to the Mineral Market Reports of U.S. Bureau of Mines, [2,3] consumption of bitumen in the United States during 1933 showed little change over the figures for 1932. Less than 1·0 per cent. of the bitumen consumed was imported, but of the total production of bitumen, about 50 per cent. was manufactured from imported crudes. Owing to substitution of cut-back bitumen for road oils in low cost types of surfacing, sales of the former materials have increased from 8·1 per cent. of the total bitumen consumption during 1930 to 21 per cent. in 1933, whilst sales of road oils show a decrease of 24·5 per cent. as compared with 1932 figures.

In connection with the history of the development of the bitumen industry, Forbes [4] gives a very comprehensive account of the earliest known references to bituminous substances.

Manufacture of Asphaltic Bitumen.

A number of papers have been devoted to the description of modern, single, or two-stage atmospheric-vacuum plants for the manufacture of bitumen. Thus Born and Nelson,[5] after brief mention of the older methods of manufacture, describe a typical modern plant in some detail, whilst another article [6] gives details of the operations of the latter type of plant. Batchelor [7] gives an account of the manufacture of steam-reduced and blown bitumens from Mid-Continent crudes by shell-still batch and single and two-stage continuous processes, and briefly describes a plant for production of cut-back bitumen. This author states that Mid-Continent bitumen

is not suitable for emulsion manufacture on account of its wax content. Manufacture of bitumen by precipitation from the crude by means of suitable precipitating solvents is briefly touched upon by Swanson and Cooke,[8] who state that a valuable type of bitumen is obtained by this method, the bitumen being free from oil and unaffected by chemical or heat reaction effects during production.

Methods of manufacture of special types of bitumen have also been described in some of the patent literature during the past year. These patents relate to processes for the production of blown bitumens,[9] a process in which the susceptibility to temperature change of bitumen is lowered by contacting the latter with a halogen in admixture with oxygen at a temperature of 450/600° F.[10]; manufacture of wax-free bitumen by separation of the constituents of an oil–wax mixture by means of a liquefied gaseous hydrocarbon and mixing the precipitated bitumen and wax-free oil [11]; recovery of bitumen from oily substances by precipitation in two stages with materials having an increased precipitating power for bitumen [12]; extraction of bitumen from asphalt rock [13]; manufacture of bitumen from cracked residue by passing the latter at a temperature of 450° F. into the vapour space of a zone containing water, the volatile constituents being thus recovered and the unvaporised material, *i.e.* bitumen, then removed and separated from water.[14] A method of cooling bitumen in order to obtain the bitumen in a granular form is also described,[15] whilst a further patent deals with the production of a bituminous road material containing 20 per cent. of chlorinated rubber.[16]

Chemical and Physical Properties of Asphaltic Bitumen.

The effect of wax on the properties of bitumen still continues to receive attention, and Müller and Pilat [17] conclude from the results of examination of Boryslaw and Polish bitumens that wax has little effect on ductility as compared with the action of large-sized asphaltic bodies of high molecular weight. These bodies, which according to the authors are not true asphaltenes, since they are only partially soluble in carbon tetrachloride, are formed during distillation in a shell still. The difference in properties of the benzine-soluble portions of two samples of Boryslaw bitumen, of 62° C. and 78° C. softening point respectively, resulting from precipitation of the asphaltenes by means of benzines of increasing specific gravity, was also investigated, and it is shown that up to a certain specific gravity of the precipitant, ductility increases, but then falls off; the softening point, however, continues to increase, and the penetration decreases as the specific gravity of the benzine is raised. The change in properties of a wax-free Polish bitumen as a result of the addition of "asphaltenes" and also of magnesium carbonate was found to depend to a great extent on the degree of subdivision of the added materials. Addition of up to 7·5 per cent. of naphthalene resulted in improved ductility, but larger amounts caused a falling off in ductility. It is interesting to note, however, that the naphthalene was still effective at a temperature of 0° C. A somewhat similar and extremely interesting line of research is described by Mack.[18] This investigator finds that asphaltenes are soluble in asphaltic resins irrespective of source, but their solubility in oily constituents of bitumen depends on the

chemical properties of the oily constituents, being soluble in oily constituents which are rich in sulphur or aromatic in character. Asphaltenes are classified as semi-colloids, since they dialize, diffuse, and have relatively low molecular weights. The author concludes from the results of viscosity determinations that sols of asphaltenes in petrolenes are liquids of high viscosity when the oily constituents are solvents for asphaltenes, but show plastic flow when the latter are insoluble in the oily constituents. Plastic bitumens are true colloidal systems of the lyophilic type, whereas viscous bitumens belong to a system falling between true and colloidal solution. Bitumens prepared from mixtures of one type of petrolenes with asphaltenes from different sources were not found to vary greatly in physical properties, and susceptibility of bitumen is stated to depend chiefly on the type of oily constituents and the viscosity–temperature relationship of the latter. Katz [19] finds from an investigation into the effect of air-blowing on the chemical composition of a series of Alberta bitumens that the amounts of oily constituents, resins and asphaltic acids, and anhydrides decrease, and the asphaltenes increase. At the same time the molecular weights of the resins increase from 733 to 1,012, and of the asphaltenes from 2219 to 4690. The amount of oxygen in products blown for 6 to 8½ hrs. at 270° C. is slight, but increases to a maximum of 1·88 per cent. in the later stages of blowing, the oxygen being mainly in the resins with small amounts in the asphaltenes. Similarly, sulphur and nitrogen is concentrated in the resins and asphaltenes. The reaction occurring in the blowing process is believed to be one of condensation followed by polymerization, thereby forming compounds of high molecular weight.

The influence of temperature on the consistency of bitumen, as measured by the A.S.T.M. tests for penetration, float test, softening point, and ductility, the Bingham–Stephens apparatus for determination of consistency and the Bingham–Murray plastometer, have been studied by Pittman and Traxler.[20] The results indicated that all bitumens which had been subjected to appreciable air-reduction exhibited quasi-viscous or pseudo-plastic flow at temperatures between 15° C. and 130° C. Very hard steam refined bitumens show similar behaviour, but to a smaller degree than air-blown bitumens of the same penetration. Rodiger [21] investigated the effect of temperature and rate of shear on the viscosity of bituminous materials with the aid of a Tsuda capillary viscometer. Mexican bitumen of 27° C. softening point (Krämer & Sarnow) obeyed the Hagen–Poiseuille Law, the viscosity of a No. 1 tar, however, was found to depend on the pressure and temperature at temperatures around 25° C., whilst tar–bitumen mixtures showed structure viscosity at 57° C., particularly with equal proportions of the constituents, but with falling temperature structure viscosity decreased and disappeared at about 30° C.

Lenhard [22, 23, 24] in a number of articles discusses the Hoepfner–Metzger system for correlating the consistencies of bituminous materials as measured by the various viscosity penetration and softening-point methods. Methods for examination of the colour of bitumen have been put forward by Wilson [25] and by Graefe [26]: in the former method a solution of the bitumen is examined in a Lovibond Tintometer, whilst in the latter method a solution of the bitumen is compared with dilute aqueous iodine solution. Both these investigators find that natural asphalts are lighter in colour than asphaltic

bitumen, Wilson finding that the colour of asphaltic bitumen depends on the hardness and origin of the bitumen, whilst Graefe finds that blown bitumens are darker than steam-refined bitumens.

Da Fano [27] states that the dropping point of tar and bitumen can be raised without appreciably altering the hardness and consistency at ordinary temperatures by treatment similar to that given in converting mineral oils to gels.

Temme [28] discusses the effect of various physical and chemical properties of bituminous materials on their behaviour when used in road construction.

The phenomenon of adhesion of bituminous binders to aggregate has been responsible for a considerable amount of work and Riedel,[29, 30, 31] continuing his investigation into the causes of adhesion, concludes, as a result of experiments in which the reduction in acidity of spindle oil after admixture and separation from finely divided $MgCO_3$, $CaCO_3$, Fe_2O_3, and Al_2O_3 was determined and water and alcoholic extracts of the residual solids examined, that hydrophobic materials react with polar compounds of the oil or bitumen to form water-insoluble compounds, which are, however, soluble in the wetting phase, hydrophilic materials on the other hand either do not react or form water-soluble compounds.

Aggregates which are hydrophobic contain an excess of basic constituents, whilst hydrophilic properties are shown when the ratio of acid to basic constituents is greater than unity.

Dahlberg [32] criticises the method of Riedel and Weber for measuring adhesion, on account of the fact that this test is made at a temperature of 100° C., and suggests that determinations should be made at 100° C., 70° C., and 50° C., and results at — 10° C. extrapolated from a curve. It is also the opinion of this investigator that adhesion is not entirely a chemical reaction, but that physical forces may also be involved. Geissler,[33] however, in reviewing the various methods put forward for measuring adhesivity, deals with criticisms which have been made in connection with the Riedel method adopted by the D.I.N. It is stated that examination of the method by various investigators has shown in general satisfactory reproducibility and good agreement with practice. Moll's view that the size of the aggregate has an influence on the results is claimed to be unsubstantiated, whilst, in reply to Dahlberg's objection, it is stated that results obtained at room temperature agree exactly with the results obtained at 100° C., and that the latter temperature was adopted in order to speed up the test. This author concludes from the examination of a number of stones and binders that the adhesion of bitumen or tar to a given stone differs only slightly, but that stones of the same type but from different sources may show entirely different behaviour. Adhesion is stated as a rule to increase with time, and it is believed that the chemical composition of the aggregate is the principal factor of influence. Swelling of binder-stone mixtures in water is believed to be indirectly related to adhesion, since swelling occurs in mixtures of hydrophilic stones, whereas hydrophobic stone mixtures swell only slightly; this is thought to be due to displacement of the bituminous coating and consequent wetting of the aggregate by water. From an investigation into the relationship between the surface tension of bitumen and tar and adhesion Saal [34] is also of the opinion that the influence of the stone is the principal factor affecting adhesion. The loss on evaporation of liquid

bitumens by the various well-known volatility tests and the properties of the residues have been compared by Lewis [35] with results obtained by evaporation of thin films of the materials exposed at atmospheric temperatures in chambers constructed to permit of cleansed air being circulated for fifteen weeks. This author states that the loss in the distillation test more nearly approximates that occurring in the exposed films than in any other laboratory test, but that the extent to which the material is hardened is in general greater in the case of the exposure residues. The development of a ductile residue in the bitumen residue test does not necessarily indicate that the material will give a residue having ductile properties under exposure conditions. Changes in inherent characteristics which may be attributed to oxidation, polymerization, and carbonization occur to a greater extent in exposure residues, and least in distillation residues, but carbonization occurs only in laboratory, and exposure residues of those bitumens which originally contained material insoluble in carbon bisulphide and carbon tetrachloride.

Application of Asphaltic Bitumen.

Asphalt and Emulsions.—The principal application of the above materials is naturally in the construction of various types of road surfacing. It is therefore not surprising that a great many articles have been devoted to the use of bitumen in this connection.

Thus Lengerke [36] deals with the types of surfacing used in the construction of motor-roads in Germany during the last thirteen years, the behaviour of the various surfacings also being discussed. The question as to the most suitable type of surfacing for construction of motor-roads has also been responsible for articles by Neumann,[37, 38] who is of the opinion that only surfacings such as asphaltic concrete which consolidate rapidly are satisfactory for this purpose. Road construction in Italy is discussed by Klinkmann,[39] whilst the use of Stalion rock asphalts for the construction of road surfacings is dealt with by Di Renzo,[40] who describes experiments made in Milan with mastic surfacings composed of these asphalts, and by I.V.,[41] who discusses methods of constructing non-skid carpets with rock asphalt. A method of roughening compressed rock asphalt by the use of emulsion is also described by Rosenbaum.[42] Wilson, [25] in an article dealing with the respective uses of asphalt, bitumen, and tar, states that each of these materials has its own sphere of use. Methods of urban road construction are discussed by Heinrici,[43] whilst Macht [44] refers to experimental work on the Breslau–Oberschlesian arterial road. Papers in connection with low cost types of construction using asphaltic bitumen emulsion, cut-backs, and road oil have been given by Noonan,[45] Shelby,[46] and Watts.[47] Salsano [48] gives details of the maintenance of a road with emulsion, whilst the use of cut-back bitumen in modern methods of road construction is dealt with in articles by Milburn and Pauls,[49] von Skopnik,[50] and Gray.[51] Methods for production of non-skid carpets are responsible for several papers,[52, 53, 54] whilst the use of road oils is discussed in a number of papers.[55, 56, 57, 58] Temme [59] deals with the various applications of bitumen in industry, whilst a review of recent literature and patents dealing with the preparation and uses of bitumen tars and emulsion is given by Kissling.[60] Mention should also be made of the papers read at the meeting of the Permanent Association

of International Road Congresses held at Munich in September. These papers, which deal with the progress made since the Washington Congress in the preparation and use of asphaltic bitumen tar and emulsion, have, however, not yet been published.

Emulsions.—Despite the importance of the subject there appears to be a scarcity of literature in connection with the manufacture of asphaltic bitumen emulsions; this, no doubt, is due to the fact that manufacturers have their own special processes, which are carefully guarded secrets. Kissling,[60] however, as mentioned above, reviews the literature in connection with the preparation and uses of emulsions. Properties of bitumen and processes for its manufacture into emulsion are also briefly discussed by Garner,[61] who deals with the properties of emulsion as well. Plaizer [62] gives an account of the preparation of a special type of emulsion for building purposes. This author states that soap-type emulsions give bitumen films which tend to flow on warming, and consequently are not suitable for building purposes. Bitumen emulsions containing rubber and/or clay are therefore used, the effect of the rubber being to increase the softening point of the bitumen while the resistance to shearing forces is improved by the addition of clay. Latex may be added to emulsions already containing clay, but if ammonia has been used to preserve the latex, the emulsion must first be diluted with water.

In addition to the above, processes for the manufacture of emulsions are covered in the patent literature, but the patents are far too numerous to be dealt with in this report.

The use of emulsions of the surfacing dressing and grouting types in road construction has already been mentioned,[39, 42, 46, 48, 49, 53] while the use of stable types of emulsion in cold asphalt construction is discussed by Henne.[63, 64] An anonymous article [65] refers to the use of stable emulsions for impregnating soil. The treatment of freshly laid concrete and the preparation of concrete admixed with bitumen in the form of emulsion are mentioned by Krah [66] and Haegermann.[67] Finally, Temme [59] in the article previously mentioned describes the use of emulsion in the preparation of bituminous paper, containers, etc., from paper pulp.

Miscellaneous Applications of Bitumen.—One of the principal applications of bitumen apart from its use as a road binding material is, of course, in the paint and varnish industry, and articles by Schuller,[68] Blom,[69] and Hadert [70] are of interest in this connection. The latter author states that the important properties of bitumen for paint and varnish manufacture are softening point, solubility in various solvents, elasticity, wax content, viscosity, and ash content. Thurm [71] gives details of the composition of a bituminous mixture for construction of asphalt flooring. As impregnating material for roofing felts, da Fano [72] states that a bitumen, which may be asphaltic bitumen or fluxed natural asphalt, of 150–200 penetration is used, whilst for the top coating, fluxed asphalt of 10–20 penetration is employed. The bitumen should not contain more than 2·5 per cent. of wax. The subject of roofing compounds is also dealt with by Braun [73] in a review of the work discussed at a meeting of the Deutschen Gesellschaft für Mineraölforschung. Two articles [74, 75] refer to the use of bitumen for pipe protection, whilst Wilson [76] describes the preparation of mattresses of filled bitumen which are used for protecting the banks and river-bed of the Mississippi from damage

by flood. Van Heurn and Begheyn [77] give an account of the use of bitumen in rubber mixtures. Bituminous compounds for filling joints in concrete roads, roofs, etc., is the subject of an article by Platzmann,[78] whilst Bierhalter [79] mentions the use of bituminous solution as an adhesive for linoleum.

Testing and Specifications.

Although analysis and testing will be the subject of another report, it is felt necessary, in view of the large number of papers devoted to the examination of bituminous road materials, also to make brief reference to the papers in this report. Articles dealing with methods of arriving at the proportions of the various constituents of road-surfacing mixtures have been published by Bierhalter,[80] Wilhelmi,[81] and in an anonymous article.[82] Wilhelmi [83] also discusses the influence of fillers in bituminous filling compounds, paints, etc., whilst Gonell [84] reviews the papers dealing with fillers discussed at the meeting of the Deutschen Gesellschaft für Mineraölforschung. Ohse [85] describes the behaviour of various types of bituminous road surfacing laid in the Rhine province during 1924–1926, and gives results of laboratory examination of test pieces taken from the roads. Platzmann,[86] dealing with the causes of blister formation in bitumen coatings, states that this is generally due to moisture forming under the bitumen skin, but may also arise from air absorbed in the pores of the surface or inadequate drying of the undercoat when this consists of emulsion or bitumen solution. Mechanical tests on bituminous paving mixtures has been the subject of a number of papers. Thus Adam and Murdock,[87] Mantor and Wren,[88] Horsfield,[89] Zaleski,[90] Kriege and Gilbert,[91] and Zube [92] describe laboratory methods and apparatus for this purpose. Amman and Gruenewaldt,[93] Neumann,[38] Emmons,[94] and Carpenter [95] describe track testing machines. Moyer [96] gives details of an apparatus for determining skidding coefficients of road surfaces and data obtained on different types of surface. The research programme of the Deutschen Gesellschaft für Mineraölforschung is discussed by Bosenberg and Mallison.[97] Properties of bituminous binders for road construction are discussed by Temme.[98]

Specifications.—Specifications for the preparation and construction of compressed rock asphalt, and for rolled asphalt and mastic asphalt, have been issued by the British Standards Institution;[99] these specifications, which are revisions of existing specifications, cover the use of rock asphalt, fluxed natural and lake asphalt, and asphaltic bitumen. Tentative methods of test and specifications for bitumen emulsions are given in A.S.T.M. Standards,[100] whilst specifications for Asphalt Macadam surface course, Asphaltic concrete surface courses, Stone-filled sheet asphalt, Sheet asphalt binder and surface courses, and Asphalt macadam base have been issued, together with a revised edition of Manual No. 1.—Road-mix types, by the Asphalt Institute,[101] Westmeyer [102] discusses the second edition of the German Standard Specifications, D.I.N. 1995 (1934) for bitumen, tars, emulsions, and cut-back bitumens.

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SPECIAL PRODUCTS.

By C. Chilvers, B.Sc., F.I.C. (Member).

The literature of 1934 contains a number of references to paraffin wax and insulating oils, but the general feature of the year has been the steady development in the production of synthetic and other organic derivatives directly and indirectly from petroleum and natural gas. Progress in this direction is closely linked with advancing knowledge of the chemistry of petroleum and its derivatives. A very complete and valuable summary of this subject has been published by Carleton Ellis.[1] This volume gives a comprehensive account of the production, properties and uses of innumerable organic materials, for many of which petroleum may be regarded as an almost inexhaustible source. The same author has indicated the prospect of a chemical industry dependent on petroleum as raw material.[2]

Hydrocarbons and their Derivatives.

Hydrocarbons generally, and more particularly those of lower molecular weight, have been the subject of considerable investigation. Padovani[3] has shown that methane can be regarded as a potential source of hydrogen, the latter being formed on oxidation with carbon dioxide, steam or oxygen, in the presence of a suitable catalyst at 900–950° C.

Low-boiling hydrocarbons, normally gaseous at ordinary temperatures, but which can be readily condensed under pressure, *e.g.* ethane, propane and butane, which are obtained from natural and refinery gases and from the gasoline stabilisers, are finding extensive application in refining operations. (Ludwig[4] states that the benzine from hydrogenated coal is a valuable potential source of these liquid hydrocarbon gases.) Asphaltic matter is insoluble in these light paraffin hydrocarbons, so that lubricating oils can be deasphaltised by treatment with liquid ethane,[5] propane[6] or butane, under pressure. If the solution is chilled, *e.g.* by releasing the pressure when ethane is used, paraffin-wax is separated, so that the process can be applied both for deasphaltising and for dewaxing.[7, 8, 9, 10]

This refrigerating effect referred to above is also employed by Voorhees[11] to separate the paraffin hydrocarbons of relatively low anti-knock value from petroleum distillates. The latter are completely solidified by adding liquid ethane and allowing the mixture to expand, the solid then being progressively liquefied.

A new plant installed by the Skelly Oil Co. for the rectification of natural gas is designed to use propane as refrigerant.[12] This latter hydrocarbon and ethane resemble and can replace ammonia and carbon dioxide respectively in their application as refrigerants.[13] Similarly, the propane and butane leaving the stabiliser columns can be economically used for manufacturing ice.[14]

Liquid propane and butane have advantages over other solvents for

extracting fatty oils—the process being carried out at room temperature under pressure.[15]

Opinion varies as to the value of commercial butane (which consists chiefly of a mixture of butane and propane) as an automobile fuel, for, while Barnard [16] considers that it cannot be economically adapted for use in small automotive units, Newton [17] and Albright [18] give instances of satisfactory performances. Both Barnard [16] and Stockman,[19] however, consider that butane is a suitable fuel for railway service, the latter author from practical experience. Alden [20] suggests that an important outlet for much of the waste butane would be provided by raising the permissible vapour pressure of gasoline to enable a further 5 per cent. of butane to be incorporated in the fuel, although certain mechanical adjustments would be necessary to eliminate vapour-lock troubles.

Among other suggestions, Jamison and Bateman [21] propose propane as an alternative to acetylene in the steel industry, while the general industrial and domestic potentialities of propane and butane have been summarised by Brueckner.[22]

The thermal decomposition and polymerisation of hydrocarbons, particularly of the unsaturated series, give rise to a great number of other hydrocarbon products—the nature of which is governed by the conditions obtaining during the reaction. No attempt is made here, however, to cover the literature on this subject, as it is outside the scope of this report, but brief mention should perhaps be made of the formation of aromatic hydrocarbons from acetylene,[23] from natural gas [24] and from polynuclear hydrocarbons.[25] Petrov and Antzus [26] obtained gasoline containing 40 per cent. of naphthenes by hydrogenating acetylene under pressure in the presence of a nickel catalyst.

An important announcement was recently made [27] by the Standard Oil Co. that *iso*-octane—"the perfect fuel"—will soon be commercially available. A process has been devised for the production of this valuable hydrocarbon from *iso*butylene (isolated from cracking processes) in a series of stages, the ultimate step being high-pressure hydrogenation.

By the condensation of naphthalene, tetralin or coal tar oils with ethylene in the presence of aluminium chloride at 100–330° C., it is claimed [28] that lubricating oils stable to oxidation are produced. It has been known for some time that synthetic oils of high viscosity index can be obtained by condensation of unsaturated cracked paraffin wax with aluminium chloride as catalyst, or by condensing paraffins with aromatic nuclei. Such compounds are not entirely satisfactory, and Blackwood, Davis and others [29] have obtained a much-improved product by polymerising the light ends of refinery gasoline. The product, termed "Exanol," when blended in proportions up to 5 per cent. with lubricating oil, greatly increases the viscosity and the viscosity index.

There is a wide and increasing demand for *synthetic resins*, and the conjugated diolefines present in highly cracked oils can be polymerised to give valuable products of this type. In one process [30] the cracked material is treated with sulphuric acid, neutralised and steam-distilled with lime. The residue is distilled and the distillate treated with cresylic acid, formaldehyde and ammonia. In an alternative method described by Camp [31] the cracked distillate is polymerised in the presence of a metallic halide.

Resins are also formed by chlorinating high-boiling distillate from cracked petroleum tar,[32] whilst the reaction between substituted benzenes and ethylene dichloride in the presence of aluminium chloride also yields a plastic product.[33] These synthetic resins find a wide application in the paint and varnish industry, and also for the manufacture of moulded articles, for which purpose they are compounded with fillers and plasticisers.

Previous reports have dealt in some detail with the formation of *alcohols* from olefines, and this subject has again been particularly prominent in the patent literature, although there seems to be a certain redundancy about some of the claims made.

Brooks [34] has summarized the chief sources of olefine raw materials for the production of synthetic alcohols, giving the proportions of specific olefines which can be obtained from the various cracking processes. This author also reviews the methods which have been suggested for converting olefines to alcohols. The same investigator,[35] comparing the addition of sulphuric acid to propylene, pentene-1 and pentene-2 with the behaviour of the halogen acids, found that in the former case no primary esters were formed. According to Strahler and Hachtel,[36] the quantity of sulphuric acid required for the production of alcohol from ethylene is much reduced if the pressure is increased. A number of patents also cover the production of alcohols from olefines and sulphuric or other non-volatile inorganic acids,[37, 38, 39, 40, 41] relatively high pressures (1000 lb./sq. in.) being used in some cases.[42, 43] Selective absorption of olefines from mixtures by acids is effected by suitable choice of experimental conditions,[44] *e.g.* propylene is absorbed by 80–90 per cent. sulphuric acid at 20–23° C. and 10–25 atm., whilst ethylene at the same pressure is absorbed in 75–85 per cent. acid at 90–130° C.[45]

tert.-Butyl alcohol is formed from *iso*butene using dilute nitric acid containing potassium nitrate,[46] whilst trimethyl ethylene gives *tert.*-amyl alcohol in aqueous nitric acid.[47]

Hydration of olefines has also been effected by water in the presence of salts of relatively weak acids in neutral or alkaline aqueous solution or suspension.[48]

Experimental determinations have been made [49] of the equilibrium constants of the reactions between steam, ethylene, propylene and the butylenes at temperatures between 150° and 250° C. in the presence of active catalysts (acid phosphates containing manganese and boron). All the reactions were found to be exothermic, the constant diminishing with rising temperature. Sanders and Dodge [50] have also investigated the equilibrium constant of the catalytic vapour-phase hydration of ethylene using a number of catalysts at 360–380° C. and pressures 70–135 atm. Estimations are made of the maximum possible conversion of ethylene under given conditions. It is concluded that no very active catalyst has yet been developed for this reaction. Nevertheless, much of the patent literature on this subject is concerned with the choice of catalyst. Phosphoric acid [51, 52, 53] and phosphates,[54, 55] with or without the addition of other reagents, such as metals [52] or metallic oxides,[53] are frequently used, whilst claims are also made for oxides of boron, phosphorus and arsenic.[56] Special methods of preparing the catalysts are favoured in some cases, as for example incorporating the catalyst with a drying oil and heating the

mixture,[57] or rendering the catalyst mechanically stable by adding 20 per cent. of organic substance such as sucrose or gelatine [58] (which on heating to 200° C. gives a carbon residue only).

Oxygenated compounds have been prepared by Wiezevich and Frolich [59] by direct oxidation at high pressures of saturated hydrocarbons from natural gasoline. Stable hydrocarbons of low molecular weight require the action of oxygen at high temperatures and pressures, whilst the less stable compounds of higher molecular weight react at lower temperatures in the vapour phase forming lower derivatives. Oxidation may be continued for the production of acids. It is estimated by Sheely and King [60] that aldehydes and acids (containing 8 or 10 C atoms) can be commercially produced at some 10 per cent. of the present price by vapour-phase oxidation of a petroleum fraction b. pt. 165–205° C. using nitric acid vapour as catalyst. The conditions affecting the reaction have been exhaustively studied.

Dobryanskii and Margules [61] obtained amyl alcohols from pentanes by first chlorinating the latter and then converting to alcohols with sodium bicarbonate and hydrated lime at 180–195° C. The halogen derivatives, generally, of hydrocarbons are important as a starting point for the preparation of other compounds. Dichlor-ethane, -pentane and -butane were formed by direct chlorination of cracked gases by Dobryanskii and others [62] in a chloride medium in the presence of methane, hydrogen and carbon monoxide without the latter gases being attacked. Metal apparatus facilitates the reaction. Hjerke and Gruse [63] have patented a process for manufacturing ethyl chloride from petroleum refinery gases by contacting the lower-boiling constituents (ethylene, etc.) with hydrochloric acid, scrubbing with absorbent oil and distilling the product. Unsaturated monochlorides have been prepared [64] from tertiary olefines by atomising the latter with a stream of chlorine which injects the atomised oil into a chamber.

Paraffin and Other Waxes.

During recent years the demand for paraffin wax has increased considerably, largely owing to the extensive use of waxed paper and cardboard containers in place of bottles and tins. Progress in Great Britain in this direction has been slower than on the Continent and in America. Actually the imports of paraffin wax into Great Britain have steadily declined during the last few years, but the amount manufactured at British refineries must have increased considerably over the same period. In 1934 1,016,404 cwts. were imported, of which 503,358 cwts. came from the United States, 235,473 cwts. from British India and 127,920 cwts. from Poland.[65] The United States is still the chief supplier to this country, but the amount imported from British India is steadily increasing.

The constitution of paraffin wax is still a subject of research. Yannaquis [66] examined the fractions obtained from distilling a Pechelbronn wax in the cathode vacuum, and found two types of crystals—triclinic, which it is suggested are saturated cyclic hydrocarbons with long chains, and needle crystals—open-chain paraffins with short branches. Similar conclusions were reached by Müller and Pilat [67] regarding wax fractions extracted by solvents from petroleum asphalt.

A decrease in D.C. electrical conductivity with increase in temperature together with a hysteresis effect has been observed by Jackson [68] over the range 0–50° for a 45–55° C. paraffin wax. It is suggested that a liquid phase may be interspersed in a solid crystalline network, the boundary surface having greater conductivity than either phase.

The colour reversion of paraffin wax on exposure to light has been investigated both by Rabinovich [69] and by Shile and Avakova.[70] In both cases, it is concluded that this phenomenon is governed by the oil content and by the degree of refining. Rabinovich compared slabs of the material 1 cm. thick using the Stammer colorimeter. It was found that 1 hr.'s exposure to ultra-violet light was equivalent to 8 days' sunlight.

Recent applications of paraffix wax were summarized at the December meeting of the Institution by Higgs,[71] who also discussed the uses of the high-melting, micro-crystalline petroleum ceresins. A paper-waxing composition consisting of paraffin wax emulsified in sodium silicate has been described.[72] This is mixed with paper-pulp, alum being first added as precipitant. Dispersions can also be obtained using 1–5 per cent. of montan wax blended with molten rosin, together with an internal saponifying agent.[73] Such products are used as paints, for waterproofing and for impregnating compounds.

An improved process for producing chlorinated paraffin waxes has been patented by Barth.[74] The wax is chlorinated over water containing an insoluble carbonate such as magnesium or calcium carbonates, which reacts with the liberated hydrochloric acid. These products are used in the production of fatty acids, for flame-proofing materials, etc., whilst condensation products can readily be obtained.[75] (In this connection, brief mention should be made of the wax-like material obtained by chlorinating naphthalene.[76] These products have been marketed under the name "Seekay Waxes," and special flame-resisting properties are claimed for electric cable or rubber treated with them. An improvement in the wax-like character and plasticity is obtained by incorporating about 10 per cent. of resin oil or solid resin with the chlorinated product.[77] Emulsions of the latter with water have been prepared [78] using alkali oleate, casein or glue as stabiliser.)

A method for detecting paraffin wax or ceresin in beeswax is described by Vizern and Guillot.[79] The wax is saponified, and the residue mixed with sand, dried and extracted with light petroleum. If the extract exceeds 22 per cent., adulteration may be suspected. Erdheim [80] has suggested applying the Steiner viscometer for detecting the adulteration of ozokerite with paraffin, since the former has a much higher viscosity above 80° C.

In a process for the production of montan wax free from asphalt,[81] the wax is saponified with alkali, and the alcohols and soaps are dissolved out by alcohols of low molecular weight or their esters. Schmeling [82] has studied the influence of solvents on the pressure hydrogenation of montan wax, *e.g.* water, benzole, heptane, etc. The solvent moderates the reaction —the effect increasing with solvents of higher boiling point. Montan wax is useful as an emulsifier both for paraffin wax and asphalt.[73]

Insulating Oils.

A number of interesting papers and patents have appeared dealing with insulating oils. Contamination of the latter during transport and storage

is a frequent source of trouble, and the proposal has been made [83] to pickle the inside of tanks to remove oxides, and then to protect the cleaned surface with aluminium paint.

Both Calantar [84] and Velikovskii [85] claim that transformer oils of good quality can be obtained from Russian crudes by Edeleanu treatment. The latter author, however, states that a final activated clay treatment is essential to give a stable product. According to an American patent,[86] the breakdown voltage of transformer oils can be raised by adding a small amount of alkali alkoxide dissolved in alcohol, subsequently removing the latter by heating. Sludge formation is retarded in the presence of certain organic acids or anhydrides such as oleic, succinic, etc.[87]

The reactions which occur in these oils under service conditions are still incompletely understood. Chebotar [88] has investigated the oxidation of the oils under pressure. He considers that tests such as the Michie and Sligh do not give a true picture of the oxidisability of an oil, but that a direct determination of the oxygen absorbed should be made. This author notes the fall in pressure at definite intervals when the oil is heated in a bomb with oxygen at 151° C. under 300 lb./sq. in.

Boisselet and Mouratoff [89] find that the sludges from transformer oils consist only of acids and metallic soaps. These acids are probably cyclic saturated acids with a –CO group, whilst other oxygen atoms have probably entered the ring structure. Attention has been directed from time to time to the problem of purifying used transformer oils. For this purpose, Williams [90] treats the oil with alkaline active carbon, as the usual filtration or centrifuging do not remove acid constituents. A different process [91] involves spraying the oil at 60–200 lb./sq. in. and at 32–71° C. into a vacuum chamber, whereby gases and moisture are released. The recovered oil is cooled and the separated sludge removed by filtration.

An interesting paper by Clark [92] describes the use of chlorinated aromatic hydrocarbons, *e.g.* an eutectic mixture of pentachlordiphenyl and trichlorbenzene, as substitutes for transformer oils. They are stable and non-inflammable, whilst the S.I.C. and breakdown strength are much higher than for mineral oils. No acid products or sludge are formed under severe oxidising conditions. Fluorinated aliphatic hydrocarbons, preferably blended with halogenated aromatics, have also been suggested [93] as electrical insulating liquids.

There is a considerable field for research in connection with mineral oils other than transformer oils for insulating purposes. The requirements of the cable manufacturers absorb a large amount of oil annually, and, up to the present, opinions differ widely as to the most satisfactory impregnating material. Solvent processes are particularly useful for preparing heavy insulating oils. Ferris,[94] for example, fractionates with nitrobenzene and then treats with fuller's earth. Those fractions which show no increase in resistivity after 72 hrs. at 100° C. are selected for insulating oils. A patent by the Pirelli Co.[95] claims the addition of 2 per cent. of unsaturated aliphatic or aromatic hydrocarbons or their substitution products, *e.g.* derivatives of naphthalene, as a means for improving the electrical characteristics of insulating oils.

It was found by Scott [96] that with oil-impregnated insulation there is a considerable increase in endurance strength with rise in oil pressure at

power frequencies under long time application of the voltage, although no beneficial results were obtained under impulse stresses.

The incorporation of resins in mineral oil is facilitated by passing carefully dried steam through the heated medium, low-boiling hydrocarbons being added to displace oxygen.[97]

According to Eisler,[98] a current-voltage curve forms a valuable criterion of the electrical insulating properties of an insulating oil as a supplement to breakdown tests.

Horsch and Berberich [99] have described a small cell for routine electrical measurements such as power factor determinations on insulating oils.

The isolation of styrene and indene from the products obtained by the pyrolysis of Persian natural gas, by Birch and Hague,[100] is of interest because the aromatic mono- and di-olefines of this type have found an important application for filling joint boxes for high-tension cables.[101] The mobile liquid, with the addition of a plasticiser, gradually changes to a tough rubber-like solid which is an excellent dielectric. Sufficient polymerisation is initiated by heating for 2 hrs. at 120° C. Polymerised hydrocarbons of the polyvinyl group (*e.g.* polystyrene) have been blended with rubber through the agency of a halogen derivative of polynuclear aromatic hydrocarbons.[102]

Reference has already been made to the Seekay Waxes—chlorinated naphthalenes—which are used for producing flame-resisting electric cables.

Carbon Black and Silica Black.

A few patents and articles have appeared dealing with carbon black. This material can be produced by allowing a hydrocarbon flame, *e.g.* of natural gas, to impinge on a hot metal surface.[103] If the dry material is subjected to turbulent agitation, spherical granules of tenacious structure and with non-adherent properties are produced.[104] Carbon black of high colour intensity (which property increases with decreasing particle size) is obtained by increasing the ratio of secondary air to hydrocarbon gas, but maximum colour intensity does not correspond to maximum tinctorial strength.[105] Barron [106] has studied the adsorption isotherm for this material. If the latter is shaken with a mixture of polar and non-polar liquids, it is always retained in the non-polar layer after separation. A process for preparing a dispersion of carbon black in water has been patented.[107] Condensation products of aromatic hydrocarbon sulphonic acids with formaldehyde are used as dispersing agents.

Brief mention should be made of silica black—a mixture of carbon and silica produced by heating finely divided coal and siliceous material in the absence of air to 650–1100° C. and grading the product by air flotation.[108] It is used as a black pigment, as a carrier of nickel in hydrogenation processes, as an absorbent for gases, etc.

Dry-cleaning and other Solvents.

An anonymous article [109] discusses the relative merits of chlorinated hydrocarbons and the more usual type of white spirit solvent for dry-cleaning purposes. The former have greater cleaning power and other advantages, but are more toxic. A number of special soaps are frequently

added to dry-cleaning solvents to improve their cleansing action. Such products include magnesium, potassium and ammonium soaps, soft soap and ethyl acetate, gall soaps [110] and triethanolamine oleate.[111] The metallic soaps tend to check spontaneous combustion. Ashworth [112] has patented a process for recovering the solvent from the alkaline sludge; the latter is diluted with water and heated almost to boiling, when the mixture is allowed to stand until the emulsion breaks. Dirty spirit has also been cleaned by forcing acid through it.[113]

Other solvents may conveniently be included in this section. The products from the catalytic high-pressure hydrogenation of naphthenic petroleum fractions are said to be excellent solvents for synthetic resins,[114] although bubble caps made from phenol resins have been used in certain solvent recovery [115] plant. Hauck [116] has described methods for analysing technical solvents (containing aromatic hydrocarbons, benzine and terpenes) by viscosity and volume change measurements after treatment with nitric and sulphuric acids successively. To prevent the deposition of naphthalene in gas mains, a non-corrosive combustible solvent boiling between 150° and 250° C. and consisting of aromatic and unsaturated hydrocarbons with neutral oxygenated compounds is introduced into the gas.[117]

Special Lubricants.

There is an increasing tendency to add small quantities of special products to lubricating oils to improve their lubricating properties and physical characteristics. Frolich [118] proposes to add 0·25–5 per cent. of a synthetic ester such as the *iso*propyl ester of acids produced by the oxidation of paraffin wax. In a patent granted to Davis,[119] about 1 per cent. of wax tailings is added to a waxy hydrocarbon oil. The viscosity and viscosity index of lubricating oils are raised by adding 1–25 per cent. of decomposition products obtained by hydrogenating polymerized olefines such as butadiene, styrene,[120] etc. Natural and artificial resins have also been used. These compounds may also be added to benzine as surface lubricants or to wax to reduce brittleness. Aluminium stearate, asphaltic material and lard oil have been added to cylinder oils.[121] Other suggestions include the addition of the condensation products of paraffin wax or chlorinated paraffin wax with naphthalene and aluminium chloride,[122] polymerized vinyl compounds containing oxygen,[123] saturated fatty acids containing more than fifteen carbon atoms [124] (*e.g.* stearic acid), etc. Semi-solid lubricants have been prepared from mineral oil by adding natural or artificial beeswax or its essential constituents in the presence of small amounts of soap,[125] whilst mineral oils which form gels at room temperature are obtained by dissolving not less than 2 per cent. of a cellulose stearate or palmitate in the heated oil.[126] A compound which will impart a green bloom to oils has been extracted from the decomposition products of the aluminium chloride sludge obtained in the refining of petroleum oil.[127]

Cutting Oils.

Apart from a new U.S. Federal Specification there is little to report under this heading. The specification calls for a maximum water content of 10 per cent., maximum ash 3·5 per cent., and the oil must form stable

emulsions with water in any proportion without the addition of emulsifier.[128] Brief reference should be made to two general papers [129, 130] which discuss the selection of suitable cutting oils, to a scheme for laboratory examination of soluble cutting oils suggested by Halls,[131] and to a patented mixture consisting of hydrocarbon oil, free sulphur and sulphur chloride.[132]

Sulphonic Acids.

Pilat and his co-workers [133] have continued their researches on the α-, β- and γ-sulphonic acids derived from acid-refining of petroleum. They are differentiated by the solubility of the calcium salts in water and ether. According to Sereda,[134] the β acid forms an intense blue compound with an ether solution of a ferric salt. The yield of "Kontakt" is increased by adding naphthenic acids to the oil to be sulphonated,[135] although the sulphonic acids are not formed from the naphthenic acids, but from naphthenic hydrocarbons.[136] The increased yield may be due to a catalytic action [137] or to the increased solvent action of the naphthenic acids on the sulphonic acids in the distillate.

Water-soluble petroleum sulphonates are separated from neutral or alkaline acid sludge by solvents such as water and the lower alcohols.[138] The solution can be applied in a film to a smooth metal surface and the solvent evaporated, whereby laminar flakes are formed.

Naphthenic Acids.

During 1933 Pyhäla carried out a very comprehensive study of the naphthenic acids in petroleum, the summarised results of which were not available until the end of the year. The conclusions are that the proportion of naphthenic acids in different crudes varies with their origin (whether paraffinic or naphthenic) and with the method of distillation, and is greater in the crude oil distillates than in the crude itself.[139] Pyhäla considers that the naphthenic acid complex contains SO_2. These acids have been prepared by distilling mineral oil over alkali, dissolving the residue in solvent and treating with sulphuric acid.[140] The acid metal naphthenates [141] are most suitable as paint driers because they are more soluble in oil than the basic or neutral salts.

Insecticides.

The employment of petroleum products as horticultural spray insecticides has increased enormously during the last few years, particularly in the large fruit-growing areas, for example, of California. The oils used, however, have to be carefully chosen, and a good deal of work has been carried out with a view to classifying oils as regards their insecticidal or ovicidal activity. Petrov [142] has found that paraffin base oils are most suitable, aromatic hydrocarbons tending to burn the foliage. Martin,[143] however, investigating lubricating oils, concludes that the insecticidal and ovicidal properties of oil sprays as applied to dormant trees are independent of the base of the oil, of its viscosity (over the range 126–870 at 70° F.) and of its degree of refinement as represented by an unsulphonated residue of 60–100 per cent. by volume. According to Francis,[144] both concealed and exposed feeders can be controlled by petroleum distillates, the most active fraction being that distilling between 300° and 800° F.

Experiments by Cressman and Dawsey [145] show that the insecticidal efficiency of soap–oil emulsions varies directly as the amount of oil retained and directly as the concentration of oil, but inversely as the concentration of soap in the aqueous phase. Viscous emulsions containing kerosine, gas oil or lubricating oil with water and green or petroleum soap as emulsifier have been described by Savel'ev.[146] An investigation of the toxicity of kerosine, gas oil, etc., in these emulsions showed that gas oil is the most effective and causes least damage to plants.[147]

In addition to petroleum oils themselves, certain products of the petroleum industry are important either as insecticides or as adjuncts to other materials for improving the wetting and spreading properties. Calcium γ sulphonates obtained from the acid tar from treatment of heavy oil are excellent substitutes for soaps as spreaders, but naphthenates are considered by Martin [143, 148] to be less satisfactory, although, according to two Russian investigators,[149] naphthenic acid soaps and petroleum emulsions are useful for controlling coccids on citrus plants and tea bushes. Petrov and others [150] have studied the effect of saponified carboxylic sulpho acids (obtained by sulphonating gas oil or paraffin wax previously oxidised at 90–100° C. and 150° C. respectively) and of "Kontakt" as activators for spray products. A process for manufacturing a spreader or emulsifier by sulphonating lubricating oil and extracting with alcohol after dilution has been patented.[151]

Halowax has been recommended [152] for use with petroleum oil emulsions, blood albumen or casein being used as emulsifier.

Woodman's studies on emulsions in connection with spraying problems have been continued.[153]

Miscellaneous Products.

There are a number of products which do not come within the groups previously discussed, but which should be noted.

Three papers deal with the determination of *Helium* in natural gas. In one method, due to Gerling,[154] the gases are heated to a series of definite temperatures by a wire placed in the gaseous medium and the resistance is measured. The apparatus is calibrated with pure gases. In both the other methods, the gases are treated with activated charcoal at the temperature of liquid air. Helium (and a little neon) remains unabsorbed.[155, 156]

Nugey [157] describes a method for producing *White Oils* from a paraffin distillate by sulphuric acid treatment followed by neutralization and extraction with methyl alcohol to remove sulphonated oil soaps. The product is ultimately earth treated. For the same purpose, Lazar,[158] after removing the unsaturated and aromatic hydrocarbons, mixes the residue with alkali and distils in high vacuum.

Petrolatum appears to attract little attention from research workers, although it has a number of important applications. According to Meyer,[159] petrolatum for use in printing inks should be of a light amber colour and have a medium ductility and softness, whilst the viscosity should be between 60 and 70 seconds Saybolt at 210° F. and the melting point 46–49° C.

A number of interesting applications for *petroleum coke* have been suggested. Massie [160] describes a plant using pulverised coke of calorific value

15,000 B.Th.U. for steam raising. If the still residues in gas retorts are heated sufficiently to cause fusion followed by coking, the processed petroleum coke thus obtained can be successfully used in manufacturing all grades of iron.[161] A further application is in the production of activated carbon by successive carbonizations with chemicals at 300° F. and 800° F. followed by acid treatment.[162] Mixtures of petroleum coke and mineral-bearing matter are obtained by adding materials such as coal, coke or shale to the coking vessel.[163]

Anti-freeze solutions have still a large sale on the American market, and a number of patented compositions have been described, *e.g.* 65 per cent. *iso*propyl alcohol, 35 per cent. of methyl alcohol.[164] To detect dilution sufficient petroleum distillate is added to form a milky solution on admixture with more than 5 per cent. of water.[165] To neutralize any corrosive tendency, these alcohol solutions may have up to 0·5 per cent. of alkali, alkaline-earth, alkali antimonyl tartrate [166] or alkyl or aryl antimonyl tartrate [167] added to them.

A mixture of ethylene diamine and pyridine has been suggested as a *carbon remover* [168] for internal-combustion engines.

The properties of *oil-resisting rubber* have been investigated by Webster,[169] who found that, other things being equal, the degree of resistance to swelling is determined by the coefficient of vulcanisation. From experiments on the thermal decomposition of natural or butadiene rubber in the presence of aluminium chloride, Zelinskii and Kozlov conclude [170] that the polymerization of butadiene goes through the aromatic stage.

Attempts have frequently been made to improve the properties of asphalt, *e.g.* increasing the elasticity and reducing the tendency to flow by incorporating rubber with the asphalt. Von Heurn and Begheyn [171] have studied this problem, and find no useful improvement in the tendency to flow by heating below 170° C. for 5–8 hrs.

Birch [172] has prepared alkyl and aryl compounds of thallium by the action of lithium alkyls on dialkyl thallium bromides in benzene. The triphenyl, triethyl and tri*iso*butyl compounds were soluble in gasoline, but possessed only one-tenth of the anti-knock properties of lead tetra-ethyl.

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ANALYSIS AND TESTING.

By E. B. Evans, M.Sc., A.I.C. (Member).

The number of papers dealing with analysis and testing of petroleum products which has appeared in 1934 is, although large, not so great as in the period covered by the last report. The difference is largely attributable to the World Petroleum Congress held in 1933, at which many papers were presented embodying the latest methods and views of workers in various branches of the subject. In consequence of this "stocktaking," not only were a particularly large number of contributions made during the last period, but certain aspects of the subject have since received far less discussion in the literature, pending the formation of new views and the development of new methods. This applies in the cases of such matters as gum estimation, kerosine testing, and the invention of new viscometers.

The A.S.T.M. have published their annual volume of Standards on Petroleum Products and Lubricants, including the report of Committee D.2. There are a number of changes in the methods, and most of these will be mentioned in the appropriate section of those following, but a few alterations may be mentioned here. A number of tentative specifications for asphalt emulsions have been included in this year's Report,[1] and cover products for a variety of uses. Tentative specifications for fuel oils have also been included.[2] These cover six grades of fuel oil for burners from the very light volatile fuel to the heavy grade requiring considerable preheating. A suggested classification for Diesel fuels is also given in an appendix to the Committee's report,[3] and this includes mention of methods of rating such as Diesel index, cetene number, and critical compression ratio.

A proposed procedure for the determination of flash-points of viscous materials and of suspensions is published for information.[4] For discussion of the alterations in the method and apparatus for determination of the knock characteristics of motor fuels, reference must be made to another report. A number of minor alterations of an editorial character have been made to several of the methods.

The second edition of the "Significance of Tests of Petroleum Products" appeared in September 1934, and is a very useful compilation. Among the new features are discussions of coefficient of friction, extreme pressure lubricants, and tests for bituminous materials.

The classification adopted in the following part of this report is mainly based on methods of test, but in some cases where the methods used are peculiar to a certain class of product, a section is devoted to a group of such methods, *e.g.* the analysis of alcohol mixtures or bituminous materials. Information on general tests, such as colour determination or viscometry, will also be found under the appropriate heading.

There are also a number of general tests such as the determination of acidity, gravity, or sulphonic acid content which have been grouped, for convenience, under the heading "Miscellaneous Tests."

Alcohol Mixtures.

For the estimation of small amounts of hydrocarbons in admixture with the lower alcohols and acetone, Hoff [5] proposes to remove the acetone by means of alkaline formaldehyde, oxidise the alcohol with acid potassium dichromate, and extract the hydrocarbons with a known volume of petroleum spirit.

Two papers have appeared on the water tolerances of alcohol–gasoline mixtures. The method of Ormandy, Pond, and Davies [6] involves the use of two graduated vessels in which 50 and 500 ml., respectively, of the fuel are shaken with 2·5 ml. of water. From the volume of aqueous alcohol separated in the two cases, the percentage of alcohol present in the blend and the water tolerance in ml. per gallon are obtained by the use of tables provided. These tables are not applicable to mixtures containing appreciable amounts of benzole in addition, but could be extended to meet this condition. Bayley and Hopkins [7] use critical solution temperatures as the basis of their method, and include a consideration of the effects of *iso*propanol and benzene. They give curves showing the critical water contents over a range from $-50°$ to $+20°$ C.

Other papers on this subject which are of analytical importance include those of Shepherd [8] on the miscibility of methyl alcohol with petrol and benzene, of Ormandy, Pond, and Davies [9] on the miscibility of various aliphatic alcohols with petrol and hydrocarbons, and of Washburn and Spencer [10] on systems of methyl alcohol, *cyclo*hexane, and water.

Bituminous Materials.

The testing of bituminous materials has been considered at length in a recent book by Broome,[11] who deals with the physical, chemical, electrical, and mechanical tests which are employed for these substances. The mechanical testing of mixtures of mineral aggregate and bitumen and the preparation of test specimens are described by Adam and Murdock [12] and by Manton and Wren,[13] while Wilson [14] discusses the procedure employed in a road and building materials laboratory. An article in *Asphalt und Teer* [15] describes the methods employed in the Italian Road Institute.

The correlation of properties such as dropping-point and penetration by the Hoepfner–Metzger system has been criticised by Lenhard [16] (see also the section on Viscometry).

For testing the stability of bituminous road surfaces, Zube [17] describes an instrument known as the "Hveem Stabilometer." Other physical properties which have received attention are tenacity,[18] and brittle-point (Frass method).[19] A new A.S.T.M. test is a distillation method for the separation of volatile constituents from cut-back asphalts.[20]

The adhesivity of bitumen and stone seems to be partly a physical and partly a chemical phenomenon. The measurement of the property is dealt with in papers by Riedel [21] and Dahlberg.[22] A paper by Müller and St. V. Pilat [23] is of interest in connection with the determination of wax and asphaltenes in asphalt.

A general discussion of the methods of analysis of asphalt emulsions has appeared,[24] whilst Spielmann [25] describes some international aspects of emulsion testing, a certain amount of agreement having been reached

by seven countries at the Munich Conference. A resolution was taken to examine further a number of methods, with a view to publication by the international body.

A simple "lability" test for estimating the breaking tendencies of emulsions on the road, has been described by Blott and Osborn,[26] and good agreement has been obtained by different observers using the method in several different countries. Neubronner [27] describes the standard methods employed in several European countries for sedimentation tests on emulsions.

Colour and Light Stability.

Two important modifications have been made in the A.S.T.M. tentative method for the determination of colour by the Saybolt chromometer.[28] The use of the half-colour glass, which has been employed unofficially for some years, is now included in the tentative method. Another important improvement is the more accurate specification of the "daylight" lamp to be used; an alteration which should result in better agreement between the colour values obtained using daylight or a lamp as the sources of illumination. The specification for the source of light also applies to the Union colorimeter methods for the determination of the colours of lubricating oils and petrolatum.[29,30]

The requirements of a colour scale for lubricating oils are discussed by Ferris and McIlvain,[31] who use a Duboscq colorimeter with green light (filtered through a solution of copper salts). They give a formula for calculating "optical density colour."

Bargmann [32] measured the colour of paraffin wax by matching a 1-cm. thick plaque against a very dilute solution of potassium dichromate and Congo red, using a Stammer colorimeter. Resistance to deterioration in light was measured by exposing to ultra-violet light (exposure for 1 hr. to a 2·5-candle mercury vapour lamp was equivalent to 8 days in sunlight) and re-measuring the colour.

Distillation and Volatility.

A simple method for comparing the evaporation rates of petroleum thinners has been described by Rubek and Dahl,[33] who use shallow dishes with filter-paper discs in the bottom. Michels and Nederbragt [34] describe an apparatus for measuring the dew-point of natural gas.

A number of new distillation apparatus have appeared during the past year. Bosschart [35] has designed an "inverted fractionation" apparatus in which the liquids of highest boiling point may be recovered first. Fractionating equipment is also described by Tongberg, Quiggle, and Fenske,[36] Schicktanz,[37] whose apparatus uses fritted glass plates, Ralli and Smith [38] (continuous laboratory topping apparatus) and by Brückner [39] (fractionation of benzole). A column designed by Quiggle, Tongberg, and Fenske [40] may be used for determination of boiling points and boiling ranges.

The correlation of plant and laboratory procedures is discussed by Dailey, Meier, and Shaffer,[41] who describe two stills which may be used for the purpose.

Turning to vacuum distillation apparatus, we have that of Ellis [42] for

small quantities of high-boiling materials, and a column for use in refinery control.[43] In a study of the composition of oils, Louis and Larralde[44] use an apparatus working under cathode vacuum. A differential-pressure control device for use in vacuum distillation has been described by Palkin and Nelson,[45] and another fitting of the same type by Liebig.[46]

Gas Analysis.

A method for the analysis of dry refinery gases has been worked out by Happel and Robertson,[47] who use a simple distillation of the condensed gas, interpreting the results with the aid of charts to obtain the percentage of ethane, propanes, and butanes. The method is claimed to be quick and reasonably accurate.

The amount of gasoline in a wet gas may be determined by condensation in liquid nitrogen (at — 195° C.) and fractional evaporation. The method can be applied successfully to gases containing a very large amount of nitrogen (Tropsch and Mattox).[48] The same authors[49] have also investigated the analysis of gases containing olefines, and recommend the absorption of propenes and butenes with 87 per cent. sulphuric acid, determining the loss in volume and the molecular weights of the gases before and after removal of the above-mentioned constituents. Ethylene is absorbed in concentrated sulphuric acid containing the sulphates of nickel and silver. Another paper by Tropsch and Mattox deals with a method for the estimation of butadiene, which method is claimed to be both quick and accurate.[50] It depends on the quantitative absorption of butadiene by molten maleic anhydride in an apparatus jacketed with boiling water. *iso*Butene and acetylene up to 15 per cent. do not affect the accuracy of the determinations. Woodruff[51] proposes to determine the water vapour content of natural gas by observation of its (aqueous) dew-point.

Activated coconut charcoal, cooled in liquid air, absorbs all the constituents of natural gas, with the exception of helium and traces of hydrogen and neon which may be present. This fact has been made the basis of a method for determination of helium by Germann, Gagos, and Neilson.[52, 53] The method is claimed to be accurate to about 0·01 per cent. on samples containing 0·23–0·52 per cent. of helium.

The difference in the cooling rates of electrically-heated wires surrounded by air and exhaust gas, and the consequent difference in their resistances, has been used to construct an apparatus to measure directly the air–fuel ratio being used in an internal combustion engine. The analyser wires are incorporated in the arms of a Wheatstone bridge, and the instrument is calibrated to read air–fuel ratios from 10 to 15.[54]

Parker[55] discusses the detection of leaks by means of stenches. Apart from the normal supply of odorised gas, leaks can be tested for by the introduction of a liquid odorant into the line, for inspection purposes.

It is stated that large discrepancies may be found between the values for the heat of combustion of natural gas as determined in a Junkers calorimeter and as calculated from the analysis of the gas. These discrepancies appear to be due to errors in the methods of analysis and of calorimetry which are often employed.[55]

Kobe and Brookbank[56] have investigated the use of platinized silica

gel in the analysis of mixtures containing methane hydrocarbons. Oxidation of paraffins commences above a fairly critical temperature for each hydrocarbon, but it is not complete even at 400° C.

Another paper of general interest in connection with gas analysis is that of Matuszak [57] on a unitised gas analysis apparatus, the self-contained units of which can be combined as desired.

Grease Analysis.

A comprehensive survey of the manufacture, properties, and testing of greases has been published by Garlick.[58] Some of the tests, principally such physical ones as those for consistency, melting point, stability, and load-carrying capacity are discussed in more detail.

Heathcote [59] estimated carbon in graphited cup-greases by boiling with glacial acetic acid and filtering through a sintered glass crucible. Biffen [60] obtains the chemically inert components of greases by extracting with trichlorobenzene the heavy-metal soaps which are insoluble in ether. Such soaps as calcium stearate are completely soluble in boiling trichlorobenzene.

The flow of lubricating greases has been investigated by Arveson,[61] who concluded that the viscosity of the oil constituent is the most important factor in determining the apparent viscosity of greases at high rates of shear.

Several new instruments for grease-testing are described in a paper by Knopf.[62] A pressure viscometer is recommended for the control of this type of lubricant, and a viscidometer is used for determining the channelling and pick-up tendencies. The adherometer simulates conditions in the transmission gear and gives a measure of the adhesiveness of the lubricant. Bingham and Stephens [63] describe a method for measuring the consistencies of very stiff materials.

The estimation of lead in greases containing lead soaps may be readily carried out by boiling with a mixture of benzene and glacial acetic acid, the lead being separated as an aqueous solution of lead acetate, when the mixture is diluted with water. The lead is finally weighed as chromate.[64]

Hydrocarbon Analysis.

A comparative study of the methods for the estimation of olefines and aromatics has been carried out by Dănăilă, Jonescu, and Verona.[65] They favour the method proposed by Dănăilă in 1923, which involves determination of the total loss to 98·3 per cent. sulphuric acid, estimation of olefines with mercuric acetate or ozone, and thus obtaining the aromatics by difference.

Rosen and Robertson [66] use a distillation method for the analysis of stabiliser bottoms. The distillation curve is interpreted with the aid of charts prepared by the distillation of synthetic mixtures of propane, butane, pentane, and hexane. The method checks to within ½–2 per cent. on the various constituents.

A micro-method for iodine number determinations has been worked out by Ralls,[67] and involves the use of very dilute solutions, the reaction being carried out at 0° C. A comparison of the iodine and thiocyanogen methods for determining unsaturation leads to the conclusion that thio-

cyanogen is much less reactive than iodine, but that both reagents are subject to the influence of steric effects.[68]

Liddel and Kasper [69] have found that hydrocarbons may be distinguished by spectral analysis, the absorption characteristics being connected with the structure of the molecules. Primary, secondary, and tertiary linkages and also aromatic, and aliphatic compounds could be distinguished by this means. Another optical method of analysis has been worked out by Ward and Fulweiler,[70] who have investigated the specific refractive dispersions of a number of hydrocarbons of different series. They find that hydrocarbons with an aromatic nucleus or unsaturated linkages have higher values for the dispersion, and exemplify the method of analysis by the estimation of styrene in the condensate from manufactured gas.

Heinze and Zwergal [71] recommend the use of butanone as a solvent in the wax determination of oils of low viscosity. For high-viscosity oils a mixture of tricresol and chloroform is used. They work at — 21° C. and calculate the total amount of paraffin from the amount obtained in the first precipitation. In the case of asphaltic oils, they propose [72] to remove first the asphaltic material with bleaching earths. When naphthenic acids are present it is best to distil off the low-boiling constituents (up to 280° C. at 30 mm. pressure).

Lubricants.

The Indiana oxidation test seems to be in fairly wide use in the U.S.A., and in view of the interest in the method, further detail and discussion is now given.[73, 74] In this method the sludging times in hours required to form 10 mgr., and 100 mgr. sludge per 10 ml. of oil, and also the viscosity increase after oxidation can be measured. The viscosity increase is the more important figure in the case of oils of long sludging time, and viscosity determinations are carried out at 50 hr. intervals. The influence of factors such as temperature control, pressure, air rate, precipitation naphtha is discussed, and it is claimed that the sludging time should be reproducible within 10 per cent. by different operators.

Another method of this type, but using oxygen instead of air, has been developed by Guthrie, Higgins, and Morgan.[75] The stability numbers of oils are derived from the average of four factors obtained by measuring viscosity, carbon residue, precipitation number, and neutralisation number, before and after oxidation. Chernozhukov [76] oxidises oils in a Butkov bomb in the presence of oxygen, machine oils being heated for 4 hr. at 15 atm. oxygen pressure and 150° C., and motor and cylinder oils for 3 hr. at 250° C. and 15 atm. air pressure. The precipitation and acidity values are determined before and after treatment.

Weisselberg [77] prefers Kissling's original method for "tar number" determination, to a modification which involves adding boiling benzine to remove mineral oils. Weisselberg considers that tarry constituents are also extracted by the benzine.

Another paper of interest in connection with oxidation tests is that of Boisselet and Mouratoff,[78] who have examined the nature of the products of oxidation of oils by oxygen at about 155° C. They state that asphalt is not formed except at higher temperatures.

The nature and measurement of "oiliness" of lubricants are discussed

in several papers, and new machines are continually proposed for evaluating this property. British Timken [79] have designed an instrument for measuring film-strength of lubricants, which involves circulation of the oils between the testing surfaces. Greases may also be tested on this apparatus. The Voitländer–Thoma oil-testing machine is described by Erk,[80] and another machine by Bridgeman.[81] Andreev [82] measures surface tension as an index to oiliness and uses the Donnan pipette, somewhat modified. A process for testing lubricants for oiliness has been patented by Wells and Southcombe,[83] hand rotation being used and the uniformity of the motion noted.

There are five properties of extreme-pressure lubricants for which, according to Bridgeman,[84] test methods are needed, and these are load-carrying capacity, coefficient of friction, stability, tendency to cause wear and corrosiveness. Tests of nine lubricants on four machines showed that no two machines rated the lubricants in the same order, and that no machine gave ratings which agreed with service performance. Descriptions are given of the apparatus used by the Bureau of Standards.

Louis and Larralde [44] describe a method of distillation of lubricating oil in the cathode vacuum, deductions as to the origin, etc., of the oils are made from the physical properties of the fractions.

An automatic cooling cabinet for use in determining pour points of oils is claimed by Ziegenhain,[85] to enable twice as many samples to be handled in a given time as in the usual apparatus. Minor alterations have also been made to the A.S.T.M. method for cloud and pour points.[86]

Southcombe has published a further edition of his book on lubricating oils and their tests.[87]

Sulphur Determination.

A number of papers have appeared dealing with modifications of the apparatus and method for determining sulphur by the lamp method. Esling [88] has altered the form of his well-known apparatus for sulphur estimation. In its new form there is no U-bend between the bulbs (a point of weakness in apparatus of the lamp type), the absorber being fitted by means of a ground-glass joint to a lower vessel, from which alkali solution is sucked up into the absorber. A perforated glass plate is used to support the beads which fill the scrubber. Heinze and Schmeling [89] discuss methods for sulphur determination such as the lamp and quartz tube methods, and suggest some modifications. In the lamp method they determine the fuel burned by volumetric measurement, and a spiral glass coil is employed for washing the sulphur oxides from the gas. After a historical sketch of the development of the lamp method, Lilly [90] deals with the method and apparatus of Edgar and Calingaert (*I.E.C. Anal.*, 1930, **2**, 104), pointing out the advantages of this compared with the A.S.T.M. method. There must also be noted a paper by Chernov and Sobolev,[91] who carry out the combustion in a mixture of air and oxygen in a hermetically closed container.

Two minor modifications of the A.S.T.M. method have been suggested. Erven [92] uses a glass sleeve round the wick-tube to adjust the size of the flame; and Dolan [93] considers the ordinary mouth suction employed to agitate the liquid during the titration, to be neither convenient nor

hygienic, and replaces it by a three-way cock connected to the vacuum and air-supply systems.

According to Roelen and Feisst [94] the best procedure for determination of sulphur compounds in gases is to determine the total sulphur by combustion, and the sulphur after removal of sulphuretted hydrogen (by alkaline ferricyanide). An apparatus for total sulphur is described, which will burn 100–200 litres of gas per hour.

Because coating of the metal surface may occur, preventing further action of corrosive sulphur compounds, Dittrich [95] considers that copper is not a suitable metal for determining this class of compound; silver is open to the same objection, but mercury is quite suitable for use in the estimation of active sulphur.

For the estimation of sodium sulphide in spent soda solution Baldeschwieler [96] takes advantage of the fact that the lead salts of all the sulphoacids present, with the exception of lead sulphide, are soluble in ammonium acetate. The lead sulphide is filtered off, and weighed after the addition of lead acetate solution and boiling with ammonium acetate.

Viscometry.

A method for calibration of Ostwald viscometers has been described by Bury,[97] who uses the external pressure method for determining the kinetic energy correction and the internal head. The disadvantages of various types of viscometers for examining tars are discussed by Lee,[98] who has designed a series of viscometers of the upward-flow Ostwald pressure type, to cover the range of viscosities of such products. In the Ostwald viscometer proposed by Fenske and McClure [99] the upper bulb is in the same vertical line as the lower bulb. Besides a series of viscometers of this type, they also describe a pipette viscometer for low-temperature work.

The falling-sphere viscometer also received a certain amount of attention during last year. An instrument in which the ball is released electromagnetically, starting an electric clock at the same time, the clock being stopped when the ball reaches an electrode, is described by Jones.[100] Harris [101] also uses an electrical device for timing the fall. The different rates of fall of balls of different diameters is employed by Hirata and Kubo [102] for the examination of abnormal colloidal substances.

Two papers deal with the Steiner viscometer and its applications.[103, 104] Another bubble-type viscometer is described by Panyatin and Obleukhova.[105]

The conversion of times of efflux measured on the Redwood Number 1 viscometer, into absolute units, may be effected by a method described by Goode and Heath,[106] who derive an equation of the type $\frac{V}{D} = AT - \frac{B}{T}$. They consider that the value of A given by Higgins is about 5·9 per cent. too high.

The viscosity of tars is dependent on pressure at temperatures of about 25° C. and just over, according to Rödiger,[107] who used a capillary viscometer and investigated the effect of factors such as temperature and rate of shear, on the results.

There is still a great deal of interest in viscosity–temperature charts as

practical tools in obtaining and employing viscosity data. Lenhard [108, 109] discusses the Hoepfner–Metzger chart for comparing viscosities and dropping-points of tars and bitumens, whilst on lubricating oils a large number of papers must be noted. Docksey, Hands, and Hayward [110] have constructed charts for the direct determination of viscosity index from measurements at 100° F. and 200° F. or 50° C. and 100° C., expressed in centistokes. A method of reading viscosity indices from measurements at any two temperatures is available from charts constructed by Watson.[111]

New conversion equations for Saybolt seconds into absolute units are proposed by Alberheim, Konheim, and Larson,[112] who criticise the accuracy of both the Saybolt viscometer and the A.S.T.M. viscosity chart. They propose new formulæ for constructing the chart and for calculating viscosity index. Larson [113] also describes a system for classifying lubricating oils into index zones. The A.S.T.M. chart has also been criticised as being unsatisfactory for asphalts.[114]

Another chart for expressing viscosity–temperature relationships has been proposed by Grosholz [115] and a suggested chart for reading viscosity–gravity constants has also appeared.[116]

Miscellaneous Determinations.

There are a number of methods of general interest and application which are difficult to classify, and which will therefore be collected in this section.

Acidity. A procedure for determining the acidities of dark-coloured oils, depends on extraction with neutral alcohol at 50–80° C.[117] Wittka [118] suggests the use of alcohol–kerosine in certain circumstances, instead of alcohol–ether or alcohol–benzole.

Combustion Analysis. An absorption tube for use in combustion analysis is described by Leworthy,[119] and a pipette for the same purpose by Meanes and Newman.[120] Kirner [121] discusses the micro-determination of carbon, hydrogen, and oxygen.

Dielectric Constant. The use of broadcasting stations as sources of constant radio-frequency for dielectric measurements has been suggested by Wenzke.[122]

Diesel Index. The combustion characteristics of Diesel fuels may be simply evaluated by an expression involving only gravity and aniline point. This index correlates quite well with the critical compression ratio and with the ignition index of Butler.[123]

Gravity. A chart for obtaining one of the four variables, gravity of emulsified oil, gravity of dry crude, gravity of water in the emulsion, and water content of the emulsion if the other three are known, is given in a paper by Woelflin.[124] Hamilton [125] emphasises the need for including gravity in the specifications for fuel oils.

Gum Determination. The method " B," which was described in the 1932 report of A.S.T.M. Committee D.2, and which involves evaporation of the gasoline at a temperature of about 155° C., has now been raised to the status of a tentative method.[126] A program of work to develop a standard test for gum-stability has been initiated by the A.S.T.M.,[127] and will include work on the bomb, the Voorhees and the copper dish methods.

Heat of Combustion. A formula for the calculation of heats of combustion

from the results of elementary analysis, and which is said to be applicable over a wide range, is that of Vondracek and Schuster.[128] Rossini [129] discusses the determination of heats of combustion of some gaseous paraffins. (See also section on gas analysis.)

Nitrobenzene. Reduction with titanous sulphate has been proposed as a method for estimating small quantities of nitrobenzene in oils.[130]

Photometry. A "swinging-arm" photometer has been used by McMillan [131] in measuring the illumination from oil-lamps.

Molecular Weights. Alternative methods of molecular-weight determination of oils are the solvent method, using *cyclo*hexane, and the method involving determination of heats of vaporisation. The maximum difference between the results obtained by the two methods is about 7 per cent.[132]

Sampling. Proposals for standard methods of sampling have been made by the Italian Technical Committee.[133] Piper [134] suggests centrifuging as a method of obtaining samples of oil from impregnated paper. This method is said to be much more satisfactory than the mechanical or solvent extraction methods.

Sulphonic Acids. A colour reaction depending on the solubility in ether of the iron salts of β-sulphonic acids, to give green or blue-coloured solutions, is a sensitive method of detecting these acids.[135]

Surface Tension. The parallel-plate method for surface tension measurements has been investigated by Sata and Kurano,[136] who conclude that it is useful if sufficiently wide plates be used. According to Nasilov, Kusnetzova, and Govorova,[137] who examined various types of apparatus, the accuracy of surface tension measurements decreases considerably with rise of temperature. Saal [138] discusses the surface tension of bitumens and tars.

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ENGINE TESTS OF GASOLINE AND DIESEL FUEL.

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Gasoline.

The outstanding work during 1934 relating to engine tests of gasoline has been the repetition by the C.F.R. Committee, on a much larger scale than in 1932, of the Uniontown road tests.

Two years' laboratory work with C.F.R. engines has led to an accumulation of data which shows that ratings made by the Research and the Motor Methods on different fuels differ by widely varying amounts; certain fuels have the same octane numbers when tested by either method, whilst others are as much as ten octane numbers higher when tested by the Research than by the Motor Method with its higher engine speed and heated mixture.

It has been inevitable that producers of fuels having lower octane numbers by the Motor Method than by the Research Method should question the validity of a laboratory test which puts their products at a disadvantage relatively to the more temperature stable fuels, especially when selected road results did not show the same differences, and that the demand should grow for a new series of road tests to check the rather hurried work undertaken in 1932.

It is, of course, more generally realised to-day than it was a year or two ago that changes in engine design and fuels make it impossible ever to have a laboratory test for knock rating which is other than a tentative standard subject to periodical revision, and the 1934 analysis, although based on very carefully collected data, is not accepted as being more than suitable for current engine and fuel types.

In order to give the widest possible scope to the road test programme of 1934 at Uniontown, and to make it as valuable as possible, seven typical gasolines in general use in the U.S.A. were chosen, and to these were added nine experimental fuels. The term "experimental" was used to indicate that the nature of the gasoline was to be disclosed after the tests were finished, in contrast with the "branded" fuels the names of which were not published. Among the experimental fuels were included vapour-phase and liquid-phase cracked gasolines, blends of these with straight-run gasoline, blends with tetra-ethyl lead in various concentrations, a straight-run fuel of similar type but different distillation range from the high octane secondary standard used for the road tests, and a benzole blend which was included for the benefit of European producers.

The general characteristics of the gasolines were similar to types in use at present in Europe, and, in any case, the test results showed that even fairly large differences between distillation ranges had no effect on ratings as far as the correlation programme was concerned.

The cars used were all of American manufacture, and of the nineteen makes selected three were used in triplicate, so that the range approximated to car distribution on the road.

Comment has been made to the effect that American car engine cylinders are too large to be representative of British private car practice, but in this connection it must be remembered that the private cars in this country consume a much smaller part of the total gasoline used than is the case in the U.S.A., and that, for a proper average view to be obtained, it is necessary to include commercial vehicle types of engine. If this is done, there is probably little fault to find with the C.F.R. selection; the *average* results should be almost the same for all countries if every engine used for all road transport purposes is given due weight, although the wider range of cylinder sizes in use in Great Britain will lead to greater deviations between certain actual road ratings and the grand average of the road tests from all types taken together.

Engine test results obtained in the laboratory are not, and cannot be, more than an approximation to average road behaviour until all vehicle engines are of identical design and run under identical operating conditions, and a more general realisation of this fact would go far to eliminate misunderstandings regarding the meaning of laboratory ratings.

A description of the 1934 Uniontown tests was published in the *S.A.E. Journal* for September, 1934.[1]

Ratings were made by comparing the knock intensity during acceleration from 10 m.p.h. at 5 m.p.h. intervals with the intensities on blends of reference fuels selected to bracket the sample under examination, ratings being based on equal maximum knock intensities. The observers noted the knock intensities at each speed interval on a scale varying from zero knock through "trace," "light," and "medium" to "heavy." These verbal descriptions were given numerical values of 0, 1, 4, 8 and 12 respectively, and it was possible at the end of a test to plot a curve of knock intensity against road speed for each sample. Reference fuel blends of C–8 and A–3 were examined in the same way at the same time as the sample itself. An inspection of the plotted curves gave the equivalent rating of the sample in terms of reference fuel blends, the sample and reference fuel blend having the same rating when the maximum knock intensity on each was the same.

This method of rating was the one adopted during the 1932 tests, and appears to be some indication of the impression obtained by an ordinary user, but it must be remarked that the method is still only a technical observer's method of obtaining a road rating. The user, clearly, does not think in terms of graphical comparisons of fuel knock intensities, and no device which may be adopted by the technician can do more than approximate to the user's impressions. The maximum knock method takes no account, for example, of the difference to the user between two fuels which may have the same maximum knock, but which differ markedly in the speed at which knock dies out completely; it does not take into account the obvious difference between two fuels one of which knocks only in the low-speed range and the other only in the high-speed range, nor does it allow for the difference between two fuels one of which rises to a given maximum knock and then falls to extinction, whilst the other rises, falls, and then rises again to a high intensity at high speeds.

It has been suggested that the areas under the curves of knock intensity, giving a "knock integral," should be used as an indication of the users'

impression, and also that these areas should be examined on a basis of acceleration times rather than on speeds, and that a separate analysis should be made of low-speed knock for town driving and of high-speed knock for open country driving.

Mention of these alternative analytical methods emphasizes the essentially approximate nature of any one type of analysis, and criticisms of the test results made without allowance for the many different possible interpretations of both users and technical observers need to be considered with caution.

While the only official analysis issued is that of the C.F.R. Committee, the author has examined the results in terms of knock extinction speed (as far as values were obtained) and also, to a limited extent, in terms of "knock integral" values, and with reference to low-speed and high-speed knocks considered separately. With the single exception of the benzole blend, any lack of correlation between the Motor Method and the road test averages tends to be reduced as the averages are taken from several, rather than from any single method of analysis. For example, the vapour-phase gasoline, which appears to be depreciated by the Motor Method when compared with maximum knock ratings on the road, is appreciated by almost the same amount when considered from the point of view of knock extinction. The same fuel is depreciated by the Motor Method in comparison with a low-speed knock analysis and appreciated by a high-speed knock analysis.

The results of the tests in terms of maximum knock road ratings and the C.F.R. Motor Method ratings are given in the table below :—

Fuel No.	C.F.R. Motor Method Octane No.	Road Equivalent Octane No.
1	68·2	68·9
2	70·6	72·7
3	76·2	76·5
4	59·8	59·5
5	65·9	66·6
6	69·5	67·9
7	68·1	70·8
8	64·1	64·5
9	69·3	69·2
10	65·9	66·8
11	74·0	75·1
12	70·8	72·1
13	68·7	67·6
14	51·3	49·4
15	70·0	69·5
16	72·0	73·0

Bearing in mind the approximate nature of the figures from any road test, the agreement must be considered as extremely good, although laboratory tests are in progress to determine whether a still narrower spread of ratings (based on maximum knock intensities only) can be obtained by running the laboratory engines at a lower mixture temperature somewhere between the present value of 300° and 200° F.

It has been mentioned that any analysis of the road results on the benzole blend showed it to be depreciated by the Motor Method. This is

due, probably, to the fact that the bouncing pin responds to pressure effects in the cylinder as distinct from noise effects observed on the road. The use of an electrical method of knock measuring with a microphone may be a solution of this difficulty, and such a method is being examined, but until more suitable instrumentation is available, the Standardization Committee of the I.P.T. recommends the use of a correction number for ratings of benzole blends based on determination of the aromatic content of the fuel. When this correction is applied, the actual engine rating is to be given in every case and the corrected value appended for comparison. A similar type of correction is also detailed for alcohol blends which behave similarly to benzole blends.

The C.F.R. Engine.

Since the introduction of the engine as an A.S.T.M. apparatus, no changes have been made, except from the Research to the Motor Method, which affect ratings. The original design of carburettor has been abandoned in favour of a simpler type not so liable to get out of order in routine use. A new type of bouncing pin, with the pin held clear of the diaphragm and with re-designed springs and dust-shielded contacts, is also being tested, but reports on its behaviour are conflicting. A special committee has been formed to advise on detail improvements of the apparatus, subject to searching tests to ensure that no alterations affect test results.

It is now recognised by all who have undertaken correlation work that it is not advisable to use primary standards, *iso*-octane and heptane, for ordinary tests or even for referee tests, but to reserve these solely for co-operative calibrations of secondary standards, these calibrated secondaries being used for all actual tests of gasolines.

Calibrations of a given pair of secondaries against the primary standards are found to vary over a range of approximately two octane numbers depending on the particular engine used and its general condition, age, etc.

It has been suggested that each engine should be used with its own special calibration of secondaries against the primaries, but this proposal is open to two objections: first, the average operator who is not accustomed to the handling of the primary standards is liable to greater experimental errors with these fuels than when using secondary standards which are more nearly the same as the normal gasolines he is testing daily, and, secondly, the use of individual calibrations cannot eliminate engine differences arising either from unavoidable small manufacturing differences or from engine condition due to age.

Two engines may differ by, say, one octane number as regards calibration of a certain pair of secondary blends. If individual calibrations are used, these engines will give identical results when testing gasoline samples similar in sensitivity to the primary standards, but if the samples examined are similar in character to the secondary standards, the results will differ from one engine to the other by one octane number, and thus no advantage is obtained.

It is now agreed that calibrations of secondaries should be made on as many different engines as possible by co-operating laboratories, the results being examined and check tests made of widely divergent results. If

checks do not bring the stray values into line, the engines used for these tests should be fitted with new cylinders or otherwise brought into agreement with average values, and finally, the calibration determined from the average results from all reasonably concordant engines (agreeing to within two octane numbers) should be adopted and the use of primaries discontinued until a further issue of secondaries is necessary. This procedure ensures that almost all engines using the calibrated secondaries will rate all except a very few exceptionally sensitive fuels within a range of two octane numbers, and generally within a range of one number. If secondaries other than those calibrated under the supervision of the C.F.R. Committee are used, the measure of agreement will depend on the number of engines on which the alternative secondaries are calibrated.

There is growing evidence that engine age exerts a definite effect on ratings of certain fuel types, and that normal servicing is not sufficient to eliminate this effect. It is suggested that the change in heat flow through the top piston ring is an important factor, and that renewal of slack rings without re-machining of the grooves to a good flat surface may be inadequate. Whether re-machined grooves with non-standard width rings to suit would be better practice has not been examined, but it seems desirable at least to renew the rings and pistons as soon as the top ring is not completely sealing against gas pressure.

Engines at High Altitudes.

Tests are in progress to determine the effect of altitude on knock ratings and the methods to be adopted for correcting any altitude effect. The most obvious and, apparently, satisfactory method of correction is to open out the throttle valve (or the carburettor diaphragm in the new design) so that the power output at a given compression ratio is the same as that at sea level, the exhaust back pressure being raised also to sea level pressure by throttling at the exit from a large expansion box added to the standard exhaust system.

This method of correction can be applied for altitudes up to between 4000 and 5000 ft., and it seems probable that a slightly different design of cam-shaft could be made to give the necessary higher volumetric efficiency to compensate for still higher altitudes.

Reverting to the question of engine differences, while the present divergence is of the order of two octane numbers between extremes (rejecting obviously aged or faulty cylinders), work is proceeding with the object of securing closer agreement.

Aviation Gasolines.

The final reports of the C.F.R. Sub-Committee and the I.P.T. Sub-Committee dealing with the testing of aviation gasolines are not yet available, but there are indications that, with certain exceptions, the Motor Method or some slight modification will be appropriate. According to the American tests, benzole blends are among the exceptional cases, not being sufficiently depreciated by the Motor Method of test. In many cases the freezing-point specification will eliminate such fuels, but, to

include blends rich in cracked material as well as the benzole blends, a proposal has been made to apply an "acid heat" test in addition to the engine test. Such a test, which depends on measuring the temperature rise of a mixture of the sample with sulphuric acid, would eliminate any fuels containing more than a relatively small percentage of either benzole or cracked gasoline. Since it is possible that certain fuels might be satisfactory, even though they failed to meet the "acid heat" test, it seems more logical to search for better C.F.R. conditions, or to examine other methods of knock measuring than the use of the bouncing pin, than to eliminate sensitive fuels by means of a chemical test which does not indicate whether a slight additional amount of anti-knock material would make them usable products.

Diesel Fuels.

Little progress has been made towards standardization of methods of engine test for Diesel fuels during the year, and published reports of cetene numbers determined for special purposes show that there is an entire lack of correlation between one laboratory and another. The cetene number of one fuel has been variously reported as 45, 55, 60, 65, 73 and 75!

There are several reasons for the differences, among them being the use of different engine types, different measuring instruments, supplies of cetene (from different sources) not all the same in purity, and differences between test engines and test methods which include running tests, starting tests and critical compression ratio measurements.

Service data are scarce. It is known that engines of the air-cell type with heated throats are less fuel sensitive to change of cetene number than direct injection engines, although the latter have the better performance as regards fuel consumption. It seems desirable, therefore, that fuel tests in laboratory engines should be devised to reproduce direct injection engine conditions rather than air-cell conditions, unless there is very definite evidence forthcoming that the test engine used gives results which are applicable to the direct injection designs.

At the summer meeting of the S.A.E. the use of an index of Diesel fuel performance based on a function of aniline point and gravity was suggested by A. E. Becker and H. G. M. Fischer.[3] The critical compression ratio method of test on the C.F.R. engine was used for the engine tests, and it was found that a very good correlation was obtained between the Critical Compression Ratio (C.C.R.) and the product of the aniline point in degrees Fahrenheit and the A.P.I. gravity. The "Diesel Index" was defined as this product divided by 100. J. R. MacGregor, commenting on this index, gave starting test values and also ignition lag values for several of the same fuels, and his results show a much better agreement for the starting tests than for the ignition lag results. This is significant in view of the fact that C.C.R.'s or starting tests as made in the C.F.R. engine are not typical of any service condition in Diesel engines, whereas ignition lags are typical provided the compression ratio used for obtaining them has not been adjusted to values materially below those suitable for practice.

Other laboratories have found that the aniline point alone is in better

agreement with the cetene number determined by running tests in service type engines than is the Diesel Index.

It is also worth noting that the C.F.R. engine according to MacGregor's tests gives higher cetene numbers by the ignition lag method than by the starting method, whereas other tests in typical direct injection engines have shown the starting test cetene numbers to be higher than the running test values.

The simplicity of C.C.R. tests compared with running tests and their better correlation with the Diesel Index are instanced as being in favour of these criteria, but it is obviously wrong to accept simplicity and good correlation with a chemical test as justifying proposed methods rather than more difficult tests made under conditions in much closer agreement with practical conditions.

Much of the difficulty with running tests in the C.F.R. engine seems to be associated with the design of injection system used at present, there being considerable evidence of very erratic behaviour of the injection valve both with change of load and speed and even under apparently steady engine conditions.

Another indirect method of fuel rating based on correlation between C.F.R. tests and laboratory values was suggested by C. C. Moore and G. R. Kaye in a paper read before the A.P.I.[4] The engine used for correlation was of the original C.F.R. open-combustion chamber design, and steady running was obtained by the use of highly heated and supercharged inlet air—the conditions were thus not typical of service. The value proposed by these authors for indicating the ignition quality was the viscosity–gravity constant, and an additional expression was derived to extend the range of the expression for this constant as developed by J. B. Hill and H. B. Coats.[5]

The correlation curve given is in very good agreement with the engine test values published, and it has also been found to indicate closely the test results on a direct injection service type engine for a series of cuts from a given crude, the cuts ranging from gasoline to a light lubricating oil and residuum. Further data are required before the full value of this laboratory figure, easily determined from routine test data, can be estimated.

Although considerable effort is being made to find some other method than an engine test for indicating ignition quality, it is to be remembered that any such artificial method fails when doped fuels are used, and it can only be a general indication of quality unsuitable for specification purposes and always subject to a final examination in a test engine.

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